THE PREPARATION AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME VOLATILE FLUORINE COMPOUNDS

by

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ABSTRACT

The preparation of alkyl, phenyl and pentafluorophenyl derivatives of non-metallic fluorides has been attempted by reaction of a fluoride with a tetraorganotin. A smooth reaction occurred only with fluorides that are strong Lewis acids. In other cases decomposition of the organotin molecule occurred under the conditions necessary to initiate the reaction. The reactions are discussed in relation to the chemistry of organotin compounds and the Lewis acidic or basic character of the fluorides.

The reactions of bis(trifluoromethyl)peroxide with some metal carbonyls have been carried out with a view to preparing trifluoromethoxy derivatives of metal carbonyls. In most cases bis(trifluoromethyl)peroxide reacted as a fluorinating agent; where other products were formed, they were very unstable.

The nuclear magnetic resonance spectra of some polychloropolyfluorobenzenes and fluorobenzenes contain methyl, carboxylic ester and nitro substituents are described. ^{19}F-^{19}F and ^{1}H-^{19}F spin-spin coupling constants in these compounds are characteristic of the

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The effect that a ring substituent in a given position has on the ^{19}F chemical shift is modified by adjacent substituents. This has been shown also for methyl, carboxylic ester and nitro substituents. Both steric and electronic factors determine a substituent's effect on the ^{19}F chemical shift.

The ^{19}F nuclear magnetic resonance spectra of the three isomers of the 1,4-dichlorotetrafluorobutadiene, the two isomers of 3,4-dichlorotetrafluorocyclobutene-1 and of two chloropolyfluorocarbon derivatives of sulphu hexafluoride are described. The chemical shifts and coupling constants found are discussed in relation to current theories. The coupling constants of the 1,4-dichlorotetrafluorobutadiene isomers have permitted some observations on their conformations to be made.

Coloured solutions of tungsten hexafluoride in several organic donor solvents and of molybdenum hexafluoride and tantalum pentafluoride in hexafluorobenzene have been prepared. The ^{19}F nuclear magnetic resonance spectra of the molybdenum and tungsten hexafluoride solutions show the presence of hexafluorid molecules, inferring that the colours are due to charge transfer interaction. However the effect of such interaction upon the ^{19}F chemical shift of the hexafluoride is small. Evidence for the presence of lower valency states of tungsten was found in diethyl ether solutions.

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CONTENTS

INTRODUCTION

The chemistry of fluorine is very extensive as it is the most chemically reactive element known. It will combine directly with the majority of elements either at room or at elevated temperature. The great reactivity of fluorine is due in part to the low energy of the F-F bond (37.7 ± 0.2 kcal.mole^{-1}). This is far lower than the bond energies of the other halogens and has been attributed to repulsion between the non-bonding electrons of the F atoms. Also the other halogens have vacant d orbitals available for multiple bonding.

Fluorine is also the most electronegative element and so never exists in positive oxidation states. The oxidation state of fluorine, in its compounds is -1, although there is evidence that fluorine bridging can occur. The bonding in fluorides of electropositive elements is ionic but it is covalent in fluorides of electronegative elements and in binary fluorides where the heteroelement is in a high oxidation state. Non-metallic fluorides and the hexafluorides of transition metals fall into the latter classes. Although the bonding in such compounds is formally covalent, the

high electronegativity of fluorine can confer considerable ionic character on the M-F bond. Where suitable orbitals are available, multiple bonding from the F atom to the heteroatom(M) is likely to occur, in order to cancel out the positive charge on M. The small size of the F atom means that the orbital overlap will be large, so fluorine is more likely to form multiple bonds than, for example, chlorine. These factors are thought to contribute to the abnormal bond energies and bond distances found in binary fluorides e.g. in BF_3 and SiF_4.

The fluorine chemistry of carbon has been intensively studied, largely as a result of the search, during the last war, for materials that were inert to UF_6 and had properties similar to hydrocarbons. Saturated aliphatic fluorochlorocarbons are now important as refrigerants and aerosols; fluoroölefines find use for polymerisation to inert oils, greases and plastics. The stability of C_nF_{2n+2} compounds is due to the fact that the fluorine atoms shield the carbon chain, so that chemical attack at a C-C or C-F bond is virtually impossible due to steric hindrance. Aromatic fluorocarbons have recently been prepared by commercially attractive methods and their chemistry is being studied.

High resolution nuclear magnetic resonance

spectroscopy has been widely used to study both organic and inorganic fluorine compounds. It is often possible to determine the structure of a compound from its ^{19}F N.M.R. spectrum, although such assignments can be ambiguous. Information can also be obtained about the bonding in fluorine compounds from their spectra. Theoretical treatments are difficult and have been only partially successful, but much information has been obtained empirically.

The practical difficulties in handling fluorine and its compounds arise from the reactivity of many fluorides towards hydrocarbon grease and from the fact that they are generally hydrolysed by water. The driving force for the hydrolysis comes from the greater lattice energy of oxides, and the stability of HF. The latter readily attacks glass to give SiF_4 and water so only a trace of water is needed to initiate hydrolysis. Water molecules adsorbed on glass can be removed by baking it out above 250°C. under high vacuum to give anhydrous conditions for a reaction. A perfluorinated grease may be substituted for an hydrocarbon grease in a vacuum system, although such commercial greases are unsatisfactory. It is advisable to use all glass systems wherever possible.

Once the handling techniques have been mastered,

the study of fluorine compounds is rewarding, both for the preparation of new compounds and for the extension of chemical theory.

CHAPTER ONE

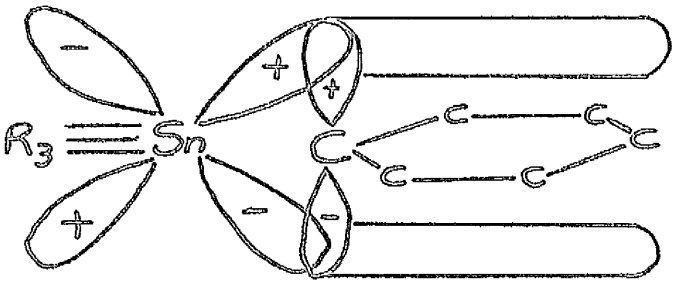
THE REACTIONS OF NON-METALLIC FLUORIDES WITH ORGANOTIN COMPOUNDS

Introduction (a) Organotin Compounds

The ground state for Group IVA atoms is denoted by ^3P (in the Russell-Saunders notation) derived from an s^2p^2 configuration (MOORE 1949). The two electrons in the subshell have coupled spins and in this state only two unpaired p electrons should be available for bonding. To form the +4 state of the atom, one of the s electrons must be promoted to a higher energy level. The resulting configuration is sp^3 for which the lowest term is a ^5S state with four unpaired electrons. For bond formation, the linear combination of the four atomic orbitals that gives the strongest bonds is the familiar tetrahedral sp^3 configuration. The +4 state has an octet of electrons and possesses low chemical reactivity.

The Pauling electronegativities of C and Sn are 2.5 and 1.8 respectively so the C-Sn bond is expected to have some ionic character (LUIJTEN, VAN DER KERK 1955). There is also evidence to suggest that in aromatic derivatives of Si, Ge, Sn and Pb the C_{aryl}-M bond has some

double bond character. CHATT and WILLIAMS (1954) found that the strengths of the acids p-$R_3M \cdot C_6H_4CO_2H$, where M = Si, Ge or Sn, as measured by the thermodynamic dissociation constant of the acid, were similar. To explain this π-bonding was postulated, by overlap of vacant d orbitals with the π-M.O. of the aromatic ring i.e.



π-Molecular orbital.

The p^{π}-d^{π}-bonding compensates for the increasing inductive effect in going from Si to Pb. These acids are stronger than the corresponding acid where M = C as π-bonding cannot occur in this case. The infra-red spectra (GRIFFITHS, DERWISH 1960) and ultra-violet spectra (GRIFFITHS, DERWISH 1959) of phenyltin compounds have both been interpreted on the basis of the C_{aryl}-Sn bond having some double bond character.

The first compounds containing Sn-C bonds were described in 1852 (LÖWIG) and since then many such compounds have been described (INGHAM, ROSENBERG, GILMAN 1960). Tetraalkyltins are colourless liquids or low melting solids, tetraaryls are colourless solids melting

above 170°C. All tetraorganotins are stable to water and oxygen.. Both alkyl and aryl compounds are easily prepared by the reaction of Grignard reagents with a tin tetrahalide (POPE, PEACHEY 1903).

Since the war the interest in polyfluoro aliphatic and aromatic systems has led to the preparation of perfluoro-alkyl and aryl derivatives of tin. Mixed alkyl(aryl)perfluoroalkyltins have been prepared by the action of CF_3I on $R_3Sn-SnR_3$ compounds (KAESZ, PHILLIPS, STONE 1960. CLARK, WILLIS 1960). Tetrakis (pentafluoro-phenyl)tin and other organotin compounds containing a C_6F_5- group have been prepared (HOLMES, PEACOCK, TATLOW 1963) by the reaction of C_6F_5MgBr with $SnCl_4$ or with alkyl(aryl)tinhalides.

The most important reaction of tetraorganotins is the cleavage of the Sn-C bond by electrophilic reagents.. This has been studied particularly using halogens and halogen acids as the resulting organotin halides are reactive and important intermediates (INGHAM, ROSENBERG, GILMAN 1960). The order of cleavage by acids of the organic groups in unsymmetrical organotin compounds has been well studied (ROSENBERG, DEPRECZENI, WEINBERG 1959; KAESZ, PHILLIPS, STONE 1960; CHAMBERS, CHIVERS 1963) and is o-tolyl $>$ p-tolyl $> CF_2{:}CF \sim$ phenyl $> CH_2{:}CH >$ $C_6F_5 >$ alkyl $>$ perfluoroalkyl. It has been suggested

(KAESZ, PHILLIPS, STONE 1960) that the main factor determining this order is the electron density round the carbon atom of the Sn-C bond, rather than the group electronegativity. The greater ease of cleavage of a phenyl, relative to an alkyl group is due to the greater electronegativity of an sp^2 carbon, relative to an sp^3 carbon (COULSON 1952).

The cleavage of the carbon metal bond in aryl derivatives of group IV elements has been studied quantitatively (EABORN, PANDE 1960). The relative rates of cleavage in the acid solvolysis $ArMR_3 + YOH \xrightarrow{H^+} ArH + R_3MOH$, increases in going from Si to Pb. The rate of cleavage of Sn relative to that of Si is 3.5×10^5. The cleavage of the C-Sn bond by aqueous perchloric acid in compounds of the type $R_3SnC_6H_4X$ (where R = Me or cyclohexyl) is enhanced when X has electron releasing properties and decreased when X is electron attracting (EABORN, WATERS 1961). A rigorous kinetic treatment however, indicates that the mechanism is not a straightforward electrophilic substitution. The cleavage of the Ar-Sn bond by iodine, although electrophilic in character, is thought to involve a π-complex between $Ar-SnR_3$ and I_2 in the rate determining step. Also the rate of cleavage is affected by the nature of R, the relative

rates of reaction being R = C_6H_{11} 5.4; Et 5.1; Me 1.0 and Ph 0.018 (BOTT, EABORN, WATERS 1963).

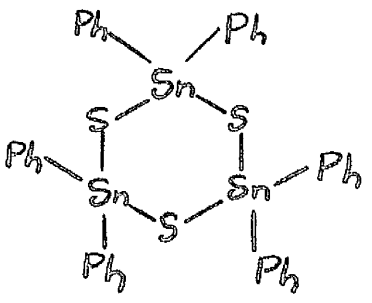
Cleavage of the C-Sn bond by a large number of reagents has been reported e.g. the halides of trivalent Group V elements (SEYFERTH 1957).

Replacement of the halogen atom (or atoms) in organotin halides proceeds very easily where the halogen is Cl, Br or I. By this method a large number of organotin derivatives have been prepared e.g. Ph_3SnLi (GILMAN, MARRS, SIM 1962) and Ph_3SnONO_2 (SHAPIRO, BECKER 1962). Hydrolysis gives the corresponding hydroxide and oxide (KUSHLEFSKY, SIMMONS, ROSS 1963). In contrast organotin fluorides are insoluble, unreactive compounds. The properties of Ph_3SnF are such that it finds use as an analytical precipitate in the analysis of fluorine. The crystal structure of trimethyltin fluoride (CLARK, O'BRIEN, TROTTER 1963) consists of long chains of Me_3Sn groups and F atoms, with only weak Van der Waals forces between the chains. The Sn—F chains are not linear and the Sn atom is apparently five co-ordinate. No evidence has been found for the existence of Me_3Sn^+ ions in the fluoride.

There is little evidence that the C-Sn bond in tetraorganotin compounds undergoes nucleophilic attack. For example no adducts are formed between pyridine

and tetraorganotins (BEATTIE, McQUILLAN 1963). Adducts (with pyridine and other donor molecules) of organotin chlorides, bromides and iodides are well known, their stability increasing with a decrease in the number of organic groups. In $Me_3SnClpy$ an X-ray structure determination has shown Sn to be five co-ordinate (HULME 1963). It has been suggested (PRINCE 1959) that nucleophilic attack results from the following equilibrium set up between the chloride (bromide or iodide) and a donor solvent (L) $L: + R_3SnX \rightleftharpoons L:SnR_3^+ + X^-$. This effect is enhanced when one (or more) of the organic groups is $-CF_3$ (CHAMBERS, CLARK, WILLIS 1961). Attack of tertiary phosphines on organotin chlorides and bromides is thought to proceed via nucleophilic attack at the Sn atom (CAMPBELL, FOWLES, NIXON 1964).

Reaction of sulphur with Ph_4Sn gives $(Ph_2SnS)_3$ and Ph_2S; it has been suggested that the first step in the reaction is nucleophilic attack by a sulphur chain at the Sn atom (SCHMIDT, DERSIN, SCHUMANN 1962). The trimer is formulated as a ring structure, viz.



but no evidence has been presented to support this. Reaction of Ph_4Sn with selenium gives $Ph_3SnSePh$. Again nucleophilic attack on Sn by Se is postulated (SCHMIDT, SCHUMANN 1963).

(b) Hydrocarbon and Fluorocarbon Derivatives of Non-metallic Fluorides

Reference to these types of derivatives of non-metallic fluorides is rare in the literature, compared to the derivatives of other halides. Alkyldifluoroboranes have been prepared (DOLLIMORE, LONG 1953) by halogen exchange between the corresponding chlorides or bromides and antimony trifluoride. Aryl and alkyl difluoroboranes have also been prepared by reaction of BF_3 with triaryl(alkyl)boroxines (McCUSKER, MAKOWSKI 1957).

Fluoromethyldifluoroborane is unstable, decomposing to give BF_3 (LAGOWSKI, THOMPSON 1959) but CF_3BF_2 which would be expected to be more unstable due to the increased electronegativity of the substituent, only decomposes slowly to BF_3 in the presence of mercury. It has been prepared by two methods (PARSONS, BAKER, BURG, JUVINALL 1961), (i) by reaction of $KB(n\text{-}C_4H_9)_2$ with CF_3I and (ii) by the reaction of B_2H_6 with CF_3SCl. Tris(pentafluorophenyl)boron has been prepared recently by the reaction of C_6F_5Li with BCL_3 (MASSEY, PARK, STONE 1963).

A number of methods for the preparation of alkyl

and aryl phosphoranes now exist, the most general being the reaction of chlorophosphines with SbF_3 or AsF_3 (SCHMUTZLER 1964). The reaction involves oxidative fluorination and is applicable unless a highly electron withdrawing substituent is present (NIXON 1963). Other reactions that have been used to prepare this type of compound include the fluorination of complexes of the type $(RPCl_3)^+ (AlCl_4)^-$ with HF (COATES, CARTER 1955). Sulphur tetrafluoride reacts with compounds containing C=O, P=O, and As=O groups to form the corresponding gem difluoride. This reaction has been used (SMITH 1960) to prepare R_nPF_{5-n} and R_nAsF_{5-n} compounds by reaction of the appropriate acid with SF_4. Alkyl and aryl phosphonitrilic fluoride derivatives (containing up to six substituents) have been prepared by reaction of $(PNF_2)_3$ with organolithium compounds (MOELLER, TSANG 1962). N.M.R. spectra of the reaction products indicate that substitution is random.

Alkyl and aryl fluorosilanes are well known, the best preparation being by halogen exchange of the corresponding chlorosilane with ZnF_2 (EMELÉUS, WILKINS 1944).

Fluoroalkyl derivatives of SF_6 and SF_4 are prepared by electrochemical fluorination of aliphatic thiols and disulphides (LOVELACE, RAUSCH, POSTELNEK 1958).

Fluoroalkyl derivatives of SF_4 have been prepared by the addition of perfluoroölefines to SF_4 (ROSENBERG, MUETTERTIES 1962). Chlorofluoro aliphatic derivatives of SF_6 are prepared by the addition of SF_5Cl across the double bond in aliphatic fluoroolefines (CASE, RAY, ROBERTS 1961); the corresponding $-SF_5$ compounds can be prepared similarly. Phenyl sulphur trifluoride has been prepared by the reaction of AgF_2 with Ph_2S_2 in an inert solvent; $PhSF_5$ was prepared by heating $PhSF_3$ with AgF_2 in a Teflon reactor (SHEPPARD 1960). 2,4-Dinitrophenyl-sulphur trifluoride results from the fluorination of the corresponding sulphide in liquid HF (CHAMBERLAIN, KHARASCH 1955).

The fully fluorinated derivatives are stable, unreactive compounds but alkyl and aryl compounds are fuming liquids that are very easily hydrolysed. The exception to this is 2,4-dinitrophenyl sulphur trifluoride which has been reported to be a stable solid.

The Reactions between Tetraorganotins and Non-metallic Fluorides

The work described in the remainder of the chapter was undertaken with a view to preparing monosubstituted alkyl, aryl and fluoroaryl derivatives similar to those already described. It was thought that reaction of the fluoride with a tetraorganotin would provide a general

route to these compounds, by the reaction:

$$R_4Sn + XF_n = R_3SnF + RXF_{n-1}$$

The driving force for the reaction would come from the high lattice energy of the trialkyl(aryl)tin fluoride.

Reaction of Tetraphenyltin with Non-metallic Fluorides

Boron trifluoride

From the reaction of Ph_4Sn with BF_3 at 140°C. the products were phenyl difluoroborane and triphenyltin fluoride. A product that decomposed at 90°C. on attempted sublimation, is formulated as triphenyltin fluoroborate, by analogy with the tetramethyltin reaction (BURG, SPIELMAN 1961) in which Me_4Sn and BF_3 reacted together to give $MeBF_2$ and Me_3SnBF_4. The latter decomposed at 100°C. giving BF_3 and Me_3SnF. The equations for the reactions in the present work can be written thus:

$$Ph_4Sn + 2BF_3 \rightarrow PhBF_2 + Ph_3SnBF_4$$

$$Ph_3SnBF_4 \rightarrow Ph_3SnF + BF_3$$

Ph_3SnBF_4 has not been reported previously. The infra-red spectrum of Ph_3SnBF_4 shows bands characteristic of a monosubstituted aromatic molecule and two strong bands at 1072 and 1020cm^{-1} (the B-F region). The band in this region in KBF_4 (due to the ν_3 vibration of the tetrahedral ion) is split into two components (EDWARDS, MORRISON, ROSS, SCHULTZ 1955). It has been suggested that band splitting indicates a lowering of symmetry of

the ion, either through interaction between the ions in the unit cell or because of a lower site symmetry of the ion in the lattice. In the infra-red spectrum of Me_3SnBF_4 the ν_3 vibration is split into three components and all seven vibrations of the BF_4^- 'ion' are infra-red active (HATHAWAY, WEBSTER 1963). On this evidence the structure has been formulated as a chain with bridging BF_4 groups. In a number of Me_3Sn compounds the infra-red spectra suggest that the anion links Me_3Sn groups with consequent lowering of the anion's symmetry (OKAWARA, HATHAWAY, WEBSTER 1963; CLARK, O'BRIEN 1963a). No evidence has been found for the existence of the Me_3Sn^+ ion in complex acid derivatives (CLARK, O'BRIEN 1963b).

It seems likely that Ph_3SnBF_4 has a covalent structure analogous to Me_3Sn compounds, although there is the possibility of delocalisation giving extra stability to the Ph_3Sn^+ cation.

The ^1H nuclear magnetic resonance spectrum of $PhBF_2$ consists of three sets of complex peaks (intensity 2:2:1); chemical shifts (on the τ scale) are 2.8, 3.1 and 3.3τ (approx.). They are assigned to the ortho, meta and para protons respectively of the benzene ring, on the basis of the peak line width, which increases with decreasing field. The spectrum shows that there is coupling between the ring and the BF_2 residue. The ^{19}F

N.M.R. spectrum consists of a broad overlapping doublet at 93.5ppm from CCl_3F (external). The '½ peak width' of the peaks is approximately 66cps. This broadening is due to ^{11}B-^{19}F and ^{1}H-^{19}F coupling and to the quadrupole relaxation effect of the ^{11}B nucleus. This quadrupole relaxation is due to the strong coupling of the ^{11}B nucleus, by means of molecular reorientations, to local electric fields, which shortens the relaxation time of the ^{11}B nucleus and causes the collapse of fine structure. Where a nucleus having spin $I > \frac{1}{2}$ is present, fine structure will be seen only if the quadrupole moment is small, or if the high spin nucleus is in a symmetric electrical environment (e.g. ^{11}B in BF_4). The shapes of spectra where a nucleus of spin ½ is coupled to one of spin 3/2 have been calculated for different values of the life time of each spin state (BACON, GILLESPIE, QUAIL 1963). The spectrum of $PhBF_2$ is consistent with this treatment.

The chemical shifts of ^{19}F nuclei in alkyldifluoroboranes have been used to describe the bonding in these compounds. Chemical shifts are shown in Table I,1.

Table I,1

^{19}F Chemical Shifts in alkyl difluoroboranes

Compound	Chemical Shift[(a)] (ppm)
$MeBF_2$	+73.6
$EtBF_2$	+78.4
$C_3H_7BF_2$	+75.8
$CH_2=CHBF_2$	+92.7
$PhBF_2$	+93.5 [(b)]

(a) Chemical shifts of alkyl derivatives for the pure liquids are measured in ppm from CCl_3F (externally) (COYLE, STONE 1960).

(b) Present work.

All resonance occurs downfield from BF_3 implying that electron density is withdrawn from the F atoms, increasing the paramagnetic shielding term (see Chs. 3 and 5). The B-F bonds have some double bond character but this is less marked in $CH_2=CHBF_2$ and $PhBF_2$, possibly due to the occurrence of C-B π-bonding.

The reaction of tin tetraalkyls and aryls with boron Lewis acids is general and has been used to prepare alkyldifluoroboranes (BRINCKMAN, STONE 1960; BURG, SPIELMAN 1961) and alkyl(aryl)dichloroboranes (NIEDENZU, DAWSON 1960; BURCH, GERRARD, HOWARTH, MOONEY 1960).

Apart from Me_3SnBF_4 no other compounds of this type have been reported as products, although in the reactions of $n\text{-}Bu_4Sn$ with BCl_3 and BBr_3 (GERRARD, MOONEY, REES 1964) in addition to $BuBCl_2(Br_2)$, butane, butenes and stannous halides were identified, suggesting that the reaction mechanism is not simple. When Me_3SnCF_3 and BF_3 react together, the product is an adduct $Me_3Sn^+(BF_3CF_3)^-$ (CHAMBERS, CLARK, WILLIS 1960). This difference in products is due to the fact that $MeBF_2$ and $PhBF_2$ are weaker Lewis acids than BF_3, whereas CF_3BF_2 is stronger. Salts of the $CF_3BF_3^-$ ion have been prepared and the tetrahedral nature of the ion established by N.M.R. spectroscopy (CHAMBERS, CLARK, REEVES, WILLIS 1961). $CF_2{:}CFBF_2$ has been prepared by the reaction of BF_3 with $(CF_2{:}CF)_2SnMe_2$ (STAFFORD, STONE 1960).

Phosphorus pentafluoride

From the reaction of Ph_4Sn with PF_5 at 135°C. phenyltetrafluorophosphorane and triphenyltin fluoride were isolated. The ^1H nuclear magnetic resonance spectrum of $PhPF_4$ consisted of a single peak (broadened) at 3.0τ due to the ring protons. The ^{19}F N.M.R. spectrum was a doublet centred at +56.5ppm from CCl_3F (external), the separation of the doublet peaks being 970cps. The values of the coupling constants in $PhPF_4$ reported by MUETTERTIES, MAHER and SCHMUTZLER (1963) are J_{PF} = 963cps,

$J_{HF} < 0.5$cps. These authors have discussed the stereochemistry of alkyl and aryl phosphoranes using N.M.R. spectroscopy as a structural probe. For RPF_4 compounds the characteristic ^{19}F spectrum is a doublet; consistent with a tetragonal pyramidal structure where R occupies the apical position. However the PF_5 molecule, which has been shown to have a trigonal bipyramidal structure by electron diffraction studies (BRAUNE, PINNOW 1937; MUETTERTIES 1964), shows no fine structure due to non-equivalent ^{19}F nuclei in its N.M.R. spectrum. Intra-molecular exchange of the F atoms has been proposed to explain their equivalence (BERRY 1960) and a similar exchange mechanism is possible for RPF_4 compounds, if the R substituent occupies an equatorial position in a trigonal bipyramidal structure. The intermediate in such an exchange is a tetragonal pyramid with R at the apex. In addition, the chemical shifts of ^{19}F nuclei in RPF_4 compounds lie between the shifts of the equatorial and apical nuclei in R_3PF_2 and R_2PF_3 compounds, whose stereochemistry (trigonal bipyramidal) is strongly inferred from their spectra.

Although no compound containing the PF_6^- ion was isolated from the reaction of Ph_4Sn with PF_5, the formation of such an unstable compound is indicated by the strong bands at 909 and 877cm^{-1} in the infra-red

spectrum of the reaction residue. The ν_3 vibration of the PF_6^- ion in KPF_6 occurs at 845cm^{-1} (PEACOCK, SHARP 1959) so a lowering of symmetry of the PF_6^- ion analogous to that in Ph_3SnBF_4 is indicated.

Sulphur tetrafluoride

The only products isolated from the reaction of Ph_4Sn with SF_4 were benzene (yield 11% based on the reaction of one mole of Ph_4Sn) and a small amount of triphenyltin fluoride. A brown tarry substance extracted from the reaction residue had an infra-red spectrum characteristic of a monosubstituted aromatic molecule but could not be characterised. Variation of the reaction conditions did not produce a smooth reaction and it seems that the aromatic ring is attacked, producing polymeric species.

Organotin compounds in the +2 oxidation state polymerise very easily (JENSEN, CLAUSON-KASS 1943); the polymer $(Me_2Sn)_n$ has been shown to contain cyclic and linear hexamer polymers that have Sn-Sn bonds (MORGAN 1963). When tetraethyltin and hexaethylditin are irradiated with ultra-violet light, or allowed to react with $AlCl_3$, dark red polymeric organotin compounds are formed (RAZUVAEV, VYAZANKIN, SHCHEPETKOVA 1962). These are decomposed at 200°C. evolving ethane, ethylene and butane and leaving a paramagnetic residue. Ring systems

containing tin and sulphur also give rise to red compounds (POLLER 1963). The mechanism of the SF_4 reaction described here, while it might involve the formation of polymeric species, is not clear.

Sulphur hexafluoride

The reaction of Ph_4Sn with SF_6 gave benzene, Ph_3SnF and SF_4 as the identified products. A brown tar similar to that from the SF_4 reaction was also obtained. SF_4 probably resulted from the thermal decomposition of S_2F_{10} which was present as an impurity in the SF_6. This decomposition is thought to proceed via the formation of SF_5 radicals (TROST, McINTOSH 1951). Whether this plays any part in the reaction with Ph_4Sn is not clear, but fluorination of the tin and ring breakdown are involved.

Silicon tetrafluoride, Phosphonitrilic fluoride trimer

The reactions of Ph_4Sn with SiF_4 and with $(PNF_2)_3$ gave benzene and triphenyltin fluoride both in low yield. No other hydrogen containing species were identified.

Pentafluorosulphur chloride

The reaction of SF_5Cl with Ph_4Sn was very vigorous and from the products isolated it was apparent that complete breakdown of Ph_4Sn had occurred. Both sulphur and carbon were isolated in significant quantities. The other products could not be identified, but a yellow liquid isolated contained fluorocarbon groups and possibly

sulphur. A brown tar was again obtained and also a brown solid that was neither Ph_4Sn nor Ph_3SnF.

Arsenic pentafluoride

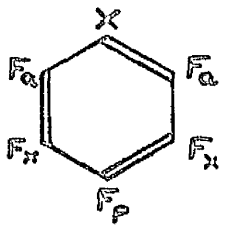
Reaction of Ph_4Sn with AsF_5 gave almost quantitative reduction of AsF_5 to AsF_3. Neither Ph_4Sn nor Ph_3SnF were isolated from the reaction products, the other product being a high melting brown solid, soluble in polar organic solvents to give dark red solutions. This solid appeared not to be crystalline.

Reactions with Tetrakis(pentafluorophenyl)tin

Sulphur tetrafluoride

The reaction of $(C_6F_5)_4Sn$ with SF_4 at 130°C. gave tris(pentafluorophenyl)tin fluoride in 31% yield (based on the reaction of one mole of $(C_6F_5)_4Sn$. This compound has not been reported previously and like Ph_3SnF, is very unreactive, being unaffected by ethanolic base after several hours. The other product isolated was a red or yellow liquid. Infra-red spectra of samples of these liquids were identical, so they were assumed to be the same compound. The presence of a C_6F_5- group is shown by its infra-red spectrum (see Table I,2) and by its ^{19}F nuclear magnetic resonance spectrum. This consists of two complex sets of peaks and a 1:2:1 triplet, the spectrum characteristic of a C_6F_5X molecule. This was analysed (see Ch.3) and the following parameters were

obtained.



Chemical shifts (relative to CCl_3F externally): F_a at 143.5, F_x at 164.2, F_p at 159.0ppm.

Coupling constants: $J^o_{F_xF_p} = 20.5$, $J^o_{F_aF_x} = \pm 21.3$, $J^p_{F_aF_x} = \mp 5.9$,

$$\left.\begin{matrix} J^m_{F_aF_a} \\ J^m_{F_xF_x} \end{matrix}\right\} = \begin{cases} 5.0 \\ 2.3 \end{cases} \text{ cps.}$$

In addition to the splittings due to these coupling constants, the peaks in the multiplet due to F_a are further split into doublets, separation 1.0cps. and those in the multiplet due to F_x are split into doublets of separation 0.9cps. One explanation of this would be that X couples with the ortho and meta F nuclei in the ring.

The ^{19}F N.M.R. spectrum of $(C_6F_5)_4Sn$ in benzotrifluoride solution shows three broad signals that were assigned as follows: chemical shifts (relative to CCl_3F), ortho F, 122.2; meta F, 159.2 and para F, 147.7ppm. The triplet separation is 19.2cps. The factors influencing chemical shifts in polyfluorobenzene compounds are discussed in Ch.3.

Analysis of the red liquid corresponds approximately

to $(C_6F_5)_2Sn$ but the physical evidence does not support this. Organotin(II) compounds are solids, generally yellow, forming yellow to red solutions in organic solvents. They polymerise readily on standing, probably by way of the vacant Sn p orbital not used in sp^2 hybridisation (GILLESPIE, NYHOLM 1957) but the liquid prepared here showed no sign of polymerising. A reaction did take place in air, the resulting colourless oil showing bands characteristic of a C_6F_5- group in its infra-red spectrum. Although tin has magnetic isotopes (^{117}Sn, ^{119}Sn) that could couple with ^{19}F nuclei, the chemical shifts of the ^{19}F nuclei in $(C_6F_5)_4Sn$ are not the same as those in the red liquid. Large downfield shifts of ortho ^{19}F nuclei have been reported in C_6F_5X compounds, where X is a metal (BOURN, GILLIES, RANDALL 1963) but no such shift was found in the spectrum of the red liquid.

The reaction of $(C_6F_5)_4Sn$ with SF_4 is sensitive to the proportion of reactants used. When the amount of SF_4 was increased decomposition took place, carbon being isolated from the reaction residue. The volatile fraction appeared to be a mixture of fluorocarbons.

Table I,2 shows the infra-red spectra of some C_6F_5- compounds. The positions of the ring vibration in the compounds studied here agree well with previous work

Table I.2

Infra-red spectra of some C_6F_5- compounds

Compound	State	Ring vibration cm^{-1}	C-F Stretching vibration cm^{-1}
[a] C_6F_6	vapour	1536	1021 1003
[a] C_6F_6	liquid film	1531	1018 994
[a] C_6F_5OH	vapour	1522 1543(doublet)	1016 994 978
[a] C_6F_5OK	mull	1479 1497	1009 974
[b] $(C_6F_5)_4Sn$	mull	1515 1475 1458(sh)	1089 1076 966
[b] $(C_6F_5)_3SnF$	mull	1518 1493 1477 doublet	1094 1082
[b] red liquid	vapour	1511 1524(sh)	1103 1029 1006 985 884
[b] liquid exposed to moist air	liquid film	1508	1098 1010 986 883

(a) BIRCHALL, HASZELDINE 1959.

(b) Present work.

but there are additional strong bands in the region 850-1000 cm^{-1}.

Boron trifluoride and phosphorus pentafluoride

There was no reaction between $(C_6F_5)_4Sn$ and BF_3 under the conditions tried and reaction with PF_5 proceeded only with difficulty to give breakdown of the C_6F_5- ring. The volatile product had an infra-red spectrum identical with the decomposition products from the SF_4 reaction. The other product was a small amount of $(C_6F_5)_3SnF$.

The non-reaction of BF_3 and PF_5 is surprising as the corresponding reactions with Ph_4Sn proceed smoothly. It seems likely that the group electronegativity of C_6F_5- is little different from that of phenyl. Mössbauer studies on $(C_6F_5)_4Sn$ suggest that the electronegativity of the C_6F_5 group is approximately the same as that of bromine (HOLMES, PEACOCK, TATLOW 1963) and nuclear magnetic resonance studies on the compounds Et_2SnX_2, where X=C_6F_5,Cl,Br or Et, indicate that the electron withdrawing power of X decreases in the order Cl $>$ C_6F_5 $>$ Br $>$ Et (MASSEY, RANDALL, SHAW 1963). Pentafluorophenyldifluoroborane has been prepared by the reaction of $Me_3SnC_6F_5$ with BF_3 in carbon tetrachloride (CHAMBERS, CHIVERS 1963). It is possible that the lack of reaction with $(C_6F_5)_4Sn$ is due to steric hinderance by the bulky C_6F_5- groups.

Reaction of Sulphur Tetrafluoride with Tetraalkyltin Compounds

$n\text{-}Bu_3SnF$ has been reported to be one of the products from the reaction of $n\text{-}Bu_4Sn$ with SF_4 at room temperature (KEMMITT 1962). In the present work, using similar reaction conditions, the volatile products were a mixture of hydrocarbons. The reaction of $n\text{-}Pr_4Sn$ with SF_4 gave $n\text{-}Pr_2SnF_2$ and a mixture of hydrocarbons as products. An orange solid formed when $n\text{-}Pr_4Sn$ and SF_4 were condensed together at $-180^{\circ}C$. is possibly an adduct. However any adduct formed is very unstable, as no evidence for its existence was found at higher temperatures. In these reactions decomposition of the alkyltin molecule must occur.

Mechanism of the Reactions

Little can be said regarding this except that a smooth reaction occurs only with the reactions of BF_3 and PF_5 with Ph_4Sn. Both BF_3 and PF_5 are strong Lewis acids, having very good acceptor properties. However, the compounds formed between BF_3 and donors such as amines, ethers etc. (GREENWOOD, MARTIN 1954) are more stable than the corresponding compounds of PF_5 (MUETTERTIES, BITHNER, FARLOW, COFFMAN 1960). Ph_3SnPF_6 is therefore likely to be more unstable than Ph_3SnBF_4. AsF_5 is a strong Lewis acid, of the same order of

strength as BF_3 in liquid hydrogen fluoride (CLIFFORD, BEACHELL, JACK 1957). However, As(V) is reduced to As(III) more easily than P(V) is reduced to P(III) (O'DONNELL 1962) and AsF_5 is a good fluorinating agent (e.g. PERKINS 1951). In the reaction of AsF_5 with Ph_4Sn, reduction to AsF_3 takes place preferentially to the formation of $PhAsF_4$.

Although SiF_4 shows acceptor properties, it is a weaker Lewis acid than other tetrafluorides e.g. SnF_4 (MUETTERTIES 1959) and is much weaker than BF_3. Phosphonitrilic fluoride trimer shows both acceptor and donor properties, reacting with dimethylamine (PADDOCK 1963) and also with acceptor molecules (SCHMULBACH 1962). Reaction of both these weak Lewis acids with Ph_4Sn gives benzene as the main product.

All three sulphur fluorides tried, produced breakdown of the Ph_4Sn molecule. With SF_4 and SF_6 the products were benzene, Ph_3SnF and possibly an aryl-tin polymeric species. SF_4 can function both as a Lewis base, giving adducts with strong Lewis acids (BARTLETT, ROBINSON 1961), and as a Lewis acid. For example, with methylamine SF_4 gives $MeN{=}SF_2$ (COHEN, MACDIARMID 1963) and presumably an adduct $MeH_2N{\cdot}SF_4$ is formed furing the reaction. Although the SF_5^- ion has been reported (TUNDER, SIEGEL 1963) it exists only

in the solid state (TULLOCK, COFFMAN, MUETTERTIES 1964).

Sulphur hexafluoride, although kinetically very stable, reacts with the Lewis acids $AlCl_3$ and SO_3 to give AlF_3 and SO_2F_2 respectively (CASE, NYMAN 1962). In the reaction of Ph_4Sn with SF_5Cl, breakdown of Ph_4Sn was more complete, SF_5Cl acting as a fluorinating agent. In reactions with olefines and fluoroölefines, SF_5Cl adds across the double bond by a radical mechanism (CASE, RAY, ROBERTS 1961) but in its reaction with trimethylamine, to give an unstable adduct $SF_5Cl \cdot 2NMe_3$ (COHEN, MACDIARMID 1963), it acts as a Lewis acid.

Conclusion

This work has shown that the reaction of non-metallic fluorides with tetraorganotins does not provide a general route to alkyl and aryl derivatives of the fluorides. Only in the reactions with the strong Lewis acids BF_3 and PF_5 is the C-Sn bond smoothly cleaved. With fluorides that are weak acids, or that show basic properties, a complicated reaction takes place, perhaps involving nucleophilic attack at Sn or on the organic group.

The fact that benzene is the main product in many of these reactions cannot easily be explained. It could result from the reaction of Ph_4Sn with HF, the latter being produced by hydrolysis of the fluoride.

However, very great care was taken to ensure anhydrous reaction conditions and it was demonstrated that if such care was not taken, benzene resulted from the reaction of Ph_4Sn with PF_5.

Benzene could be a product from the decomposition of Ph_4Sn, possibly by a free radical mechanism. However, no evidence was found for the existence of biphenyl in the reaction products, and this would be expected to be one of the products from such a decomposition.

The source of the benzene cannot be stated with certainty.

EXPERIMENTAL

Preparation and Purification of the Fluorides

Boron trifluoride was bubbled from a cylinder (supplied by Imperial Smelting Co. Ltd.) through a suspension of boric oxide in conc. sulphuric acid. It was condensed at -180°C. (onto a mixture of B_2O_3 and NaF) in a U-trap fitted with a calcium chloride drying tube. This was transferred to the vacuum line and the BF_3 redistilled at -78°C. on to NaF at -196°C., taking the middle fraction. The absence of any other compounds was confirmed by its infra-red spectrum.

Phosphorus pentafluoride was prepared by heating an aryl diazonium hexafluorophosphate, Phosfluorogen A (from Ozark Mahoning Co.). This decomposes on heating as follows:- $ArN_2^+PF_6^- = ArF + N_2 + PF_5$. The aryl fluoride was condensed in a trap at -78°C. and PF_5 condensed on a mixture of P_2O_5 and NaF at -180°C. in a U-tube fitted with a drying tube. The solid collected was distilled in vacuo at -115°C. to remove SiF_4 and then distilled at -78°C. condensing the middle fraction on to NaF at -196°C. A gas infra-red spectrum confirmed that this was PF_5 only.

Sulphur tetrafluoride was prepared by the reaction of sulphur dichloride with sodium fluoride in refluxing

acetonitrile (TULLOCK, FAWCETT, SMITH, COFFMAN 1960). SF_4 could be conveniently prepared on 100g. scale and be stored in a stainless steel cylinder. The purity obtained by this method is about 90%, the chief impurities being thionyl fluoride, hydrogen fluoride and sulphur dichloride. For use in this work SF_4 was distilled from the cylinder in vacuo and condensed on NaF. It was then purified by making the adduct BF_3SF_4, pumping off all volatile impurities, then decomposing the adduct with well-dried ether (BARTLETT, ROBINSON 1961). Purity was confirmed by gas infra-red spectroscopy. Alternatively SF_4 from the cylinder was distilled in vacuo on to NaF to remove HF and then used without further purification. The impurities in this case were SOF_2 and traces of SCl_2.

Sulphur hexafluoride was prepared by burning sulphur in a stream of fluorine diluted with nitrogen (DODD, ROBINSON 1955). SF_4 and SOF_2 were removed by vacuum distillation of the product at -115°C. The product that remained was distilled at -30°C. on to NaF, taking the most volatile fraction. A gas infra-red spectrum of this showed bands characteristic of SF_6 (LAGEMANN, JONES 1951) and disulphur decafluoride (DODD, WOODWARD, ROBERTS 1957). It was not possible to effect complete separation of these compounds so the SF_6 used contained some S_2F_{10} as impurity.

Silicon tetrafluoride was prepared by the reaction of fluorosulphuric acid with silica at 100°C. (BELF 1955). It was condensed on to NaF and purified by vacuum distillation in a manner similar to BF_3. An infra-red spectrum confirmed its purity.

Phosphonitrilicfluoride trimer (a gift from Dr. N. Paddock, University of Manchester), was distilled in vacuo at -30°C. A gas infra-red spectrum indicated its purity.

Pentafluorosulphur chloride (a gift from I.C.I. Ltd., Alkali Division) was distilled from a cylinder in vacuo on to NaF at -196°C. and redistilled at -78°C., taking the middle fraction for use. The absence of any other volatile component was shown by a gas infra-red spectrum.

Arsenic Pentafluoride was prepared by passing a stream of fluorine diluted with nitrogen over arsenic at 50°C. (DODD, ROBINSON 1955). The product (a mixture of arseni penta and trifluorides) was distilled in a stream of fluorine to convert the trifluoride to pentafluoride. SiF_4 was removed by distillation under vacuum at -115°C. and the remaining product distilled on to NaF at -60°C. A gas infra-red spectrum indicated that it was arsenic pentafluoride, together with some arsenic oxide trifluoride (MITRA 1958).

Experimental Method

The practical difficulties encountered in these reactions arose from the necessity of excluding water. The fluorides used hydrolyse very easily, only a trace of water being needed to initiate hydrolysis. If this occurs, HF is produced which attacks the glass producing SiF_4 and more water. Also the presence of HF in the reaction affects its course, as the reaction $Ar_4(Alk_4)Sn + HF = Ar_3(Alk_3)SnF + ArH(AlkH)$ goes very easily. When PF_5, which had not been purified, was reacted with tetraphenyltin the volatile product was benzene and not phenyltetrafluorophosphorane. In the reactions where benzene was the product, it was necessary to eliminate the above reaction as the source as far as possible.

Reactions were carried out in a stainless steel bomb (from Baskerville and Lindsay Ltd.) of 25 ml. capacity and having a valve fitted. This could be attached to the vacuum line by a copper connection, one end of which was fitted with a brass coupling and the other a brass B.14 socket. The bomb could be evacuated at the beginning of the reaction and the volatile fluoride condensed into it and all volatile material could be pumped from the bomb when reaction was complete. Tetraphenyltin (from Pure Chemicals Ltd.) and tetrakis

(pentafluorophenyl)tin (a gift from Dr. R. D. Peacock, University of Birmingham) were dried at 120°C. overnight before use. They were transferred to a dry box in a dessicator and the bomb was charged in the dry box. It was then evacuated and the volatile fluoride condensed in. The tetraalkyltin compounds (from Pure Chemicals Ltd.) are involatile liquids and so could not be dried in this way. They were placed in the bomb and thoroughly 'degassed' under vacuum before the fluoride was condensed in. A large excess of fluoride was used to produce the pressure needed for the reaction to proceed. The bomb was then disconnected from the line and allowed to warm up to room temperature. It was placed in an oven if reaction at elevated temperatures was required, or rocked at room temperature for the length of time desired. When the reaction time had elapsed, the bomb was cooled (if necessary) and reconnected to the vacuum line. All volatile products were pumped out, (it was sometimes necessary to pump for one or two hours to ensure complete removal) and these were investigated using the techniques described in the appendix. The bomb was opened in the dry box and the involatile compounds investigated. Until it became apparent that these were stable in moist air, all operations were conducted in the dry box or under

vacuum. It was found that an infra-red spectrum of the bomb residue gave useful information about the products. The infra-red spectra of monosubstituted aromatic compounds have been well studied (BELLAMY 1958), also the aromatic compounds of Group IV elements (NOLTES, HENRY, JANSSEN 1959). A sharp band at 9.34 μ has been found to be characteristic of the C_6H_5-Sn grouping. The spectra of compounds containing the C_6F_5- group have also been discussed (WHIFFEN 1960; BIRCHALL, HASZELDINE 1959).

Reactions with Tetraphenyltin

Boron trifluoride

Tetraphenyltin (2.7g.) was reacted with excess BF_3 at 140°C. for 40 hours. A white solid was condensed from the reaction at -196°C. This yielded a fraction that was volatile at -78°C; its infra-red spectrum was identical with that of BF_3 (GAGE, BARKER 1939). The other product was a colourless liquid (ca 1ml.), volatile at 20°C. Traces of BF_3 were removed from this by a distillation at -28°C. the products being passed through a U-trap at -80°C. (to condense the liquid), the BF_3 was condensed at -196°C. The gas infra-red spectrum of the liquid contained bands due to aromatic C-H, C=C and to B-F. Its ^1H nuclear magnetic resonance spectrum consisted of a complex signal in the aromatic

proton region and the ^{19}F N.M.R. spectrum was a broad doublet. Its molecular weight was 126 (M.W. of $C_6H_5BF_2$= 125.9). The analytical data was as follows:

found	C = 60.40,	H = 4.27,	F = 27.17
req. for $C_6H_5BF_2$	C = 57.24,	H = 4.01,	F = 30.18

The non-volatile product was a white solid from which a few mg. of a pale yellow solid were sublimed at 90°C. The sublimation was accompanied by evolution of gas. This had a molecular weight of 67.3 (M.W. of BF_3 = 67.8). Its infra-red spectrum was identical with that of BF_3. The pale yellow sublimate darkened on warming to room temperature. Its infra-red spectrum showed bands due to a monosubstituted phenyl group and two broad bands in the region 9-10μ. Insufficient of the compound was obtained for analysis.

The white residue showed bands characteristic of a C_6H_5- group in its infra-red spectrum and was unaffected by moist air. Soxhlet extraction with benzene gave a small quantity of a white solid m.p. 224°C. (lit. $(C_6H_5)_4Sn$ m.p. 224°C.). The residue not extracted with benzene was dissolved in ethanol and a white solid crystallised from the solution. An X-ray powder photograph of this was identical with that of a sample of triphenyltin fluoride (prepared by a literature method). Analytical data obtained was as follows:

Found C = 57.48, H= 4.67

$(C_6H_5)_3SnF$ req. C = 58.60, H = 4.10.

The X-ray powder photographs of tetraphenyltin and triphenyltin fluoride are completely different, thus providing an easy method for distinguishing between the two compounds. The reaction was repeated at higher temperatures (160°C., 175°C.). In each case the products were the same but the yield of $C_6H_5BF_2$ was smaller.

Phosphorus pentafluoride

Tetraphenyltin (2.0g.) was reacted with excess PF_5 (ca 4g.) at 135°C. for 20 hours. A white volatile solid was condensed at -196°C. This yielded a fraction volatile at -80°C., whose infra-red spectrum was identical with that of PF_5 (GUTOWSKY, LIEHR 1952). The other volatile product was a colourless liquid (ca 2ml.) from which the last traces of PF_5 were removed by the same technique as in the BF_3 reaction. A gas infra-red spectrum of the liquid showed bands characteristic of aromatic C-H and C=C and of P-F vibrations. The molecular weight of the compound was 162. (M.W. of $C_6H_5PF_4$ = 184). The ^1H nuclear magnetic resonance of the compound consisted of a single peak (broadened) in the aromatic proton region; the ^{19}F N.M.R. spectrum consisted of a doublet, separation = 970cps.

The liquid analysed as follows: C - 39.98, H - 2.92, P - 16.35, F - 40.52; $C_6H_5PF_4$ requires C - 39.14, H - 2.74, P - 16.83, F - 41.29. An infra-red spectrum of the white residue showed two strong bands at 909 and 877cm^{-1} in addition to those bands characteristic of monosubstituted benzenes. Sublimation was attempted, but nothing sublimed up to 120°C. nor did any decomposition take place. An infra-red spectrum after the attempted sublimation showed no bands at 909 or 877cm^{-1}, the inference being that the suspected hexafluorophosphate species had decomposed. Soxhlet extraction of the residue with benzene (for 10 hours) and crystallisation of the solution gave a white solid m.p. 224°C. (lit. $(C_6H_5)_4Sn$ m.p. 224°C.). Further extraction of the residue with methanol and crystallisation gave a white solid that decomposed above 350°C. Its X-ray powder photograph was identical with that of triphenyltin fluoride. When tetraphenyltin was reacted with PF_5 that had not been purified as already described, the main volatile products were PF_5(+SiF_4) and a colourless liquid that had a molecular weight of 80.0 (C_6H_6 M.W. = 78.1) and an infra-red spectrum identical with that of benzene. An X-ray powder photograph of the residue after the benzene extraction was identical with that of triphenyltin fluoride.

Sulphur tetrafluoride

Tetraphenyltin (0.9g.) and SF_4 (ca 4g. estimated from the volume of SF_4 used) were allowed to react at 115°C. for 18 hours. The SF_4 had previously been purified via the BF_3SF_4 adduct. A pale yellow solid was condensed at -196°C. Fractionation of the products at -78°C. gave a volatile fraction whose infra-red spectrum was identical with that of SF_4 (DODD, WOODWARD, ROBERTS 1956). No other volatile S-F compounds were identified. The other volatile product was a colourless liquid (yield 0.1g.), molecular weight = 78.7 (M.W. C_6H_6 = 78.1). Its infra-red spectrum was identical with that of benzene. The residue from the reaction was pink; its infra-red spectrum showed bands characteristic of a monosubstituted benzene but there were no bands in the S-F stretching region. From the soxhlet extraction of the residue with benzene a small amount of a brown 'tar-like' solid was isolated. This had bands characteristic of an aryl-tin group in the 9-10μ region of the infra-red and showed two strong bands in the region 13.5 - 14.5μ, characteristic of aryl groups. No tetraphenyltin was isolated. The residue insoluble in benzene was extracted (soxhlet) with methanol. A pale pink solid was obtained which did not lose its colour on further crystallisation. The X-ray powder

photograph of this was identical with that of $(C_6H_5)_3SnF$. The reaction was carried out at different temperatures but no reaction took place below 100°C. At 100°C. (and at higher temperatures) the products were the same as those already described. Using SF_4 having thionyl fluoride as impurity made no difference to the reaction products, nor did using excess tetraphenyltin.

Sulphur hexafluoride

Tetraphenyltin (2.1g.) was allowed to react with excess SF_6 (containing S_2F_{10} as impurity) at 155°C. for 90 hours. A pale yellow solid was collected at -196°C. This yielded a fraction volatile at -78°C. the infra-red spectrum of which showed strong bands at 728, 867, 882 and 1280cm^{-1}. These correspond well with the infra-red spectrum of SF_4 (DODD, WOODWARD, ROBERTS 1956) which has strong bands at 728, 867, 889 and 1281cm^{-1}. The other volatile product was a colourless liquid (ca 1ml.) of molecular weight 77.1 (M.W. of C_6H_6 =78.1). Its infra-red spectrum was identical with that of benzene.

The residue in the bomb was pale brown and an infra-red spectrum showed no S-F absorption bands. Soxhlet extraction with benzene for 12 hours gave a brown solution from which a white solid (0.8g.) m.p. 224°C. (lit. $(C_6H_5)_4Sn$ m.p. 224°C.) was crystallised.

After removal of the benzene, a dark brown tar remained. Attempts to crystallise this failed. The infra-red spectrum was very complicated but bands characteristic of aromatic C-H and a monosubstituted aryl group were identified. The ^{19}F nuclear magnetic resonance spectrum at high Rf power showed no signal.

Extraction of the residue insoluble in benzene with methanol gave a white solid (0.3g.) that decomposed above 350°C. (lit. $(C_6H_5)_3SnF$ decomp. 357°C.). The X-ray powder photograph of this compound was identical with that of $(C_6H_5)_3SnF$. Analysis gave C - 58.91, H - 4.51; $(C_6H_5)_3SnF$ requires C - 58.60, H - 4.10.

Silicon tetrafluoride

Tetraphenyltin (1.5g.) was heated with excess SiF_4 at 110°C. for 17 hours but no reaction occurred. On heating at 140°C. for 48 hours a reaction occurred. From the volatile material condensed at -196°C. a fraction volatile at -78°C. was isolated. The infra-red spectrum of this compound was identical with that of SiF_4 (JONES, KIRBY-SMITH, WOLTZ, NIELSEN 1951). The other volatile product was a colourless liquid (50mg.) of molecular weight 78.3 (C_6H_6 M.W. = 78.1). Its infra-red spectrum was identical with that of benzene. An infra-red spectrum of the involatile, white residue showed no bands characteristic of Si-F or Si-O vibrations.

Soxhlet extraction of the residue with benzene and crystallisation gave a white solid (1.2g.) m.p. 224-6°C. (lit. $(C_6H_5)_4Sn$ m.p. 224°C.). Soxhlet extraction of the residue insoluble in benzene with methanol, for 12 hours yielded a white solid (0.1g.) that decomposed above 350°C. (lit. $(C_6H_5)_3SnF$ decomp. 357°C.). The X-ray powder photograph of the compound was identical with that of $(C_6H_5)_3SnF$. Analysis gave: C - 58.84, H - 4.51 $(C_6H_5)_3SnF$ requires C - 58.60, H - 4.10.

Phosphonitrilic fluoride trimer

Tetraphenyltin (1.6g.) and $(PNF_2)_3$ were allowed to react at 110°C. for 18 hours. A white volatile solid was condensed at -196°C. An infra-red spectrum of this showed bands due to $(PNF_2)_3$, and bands characteristic of aromatic C-H and C=C vibrations. Complete separation of the components by fractional distillation was unsuccessful, although partial separation was effected by distillation through the U-trap at -65°C. The 'molecular weight' of the most volatile fraction at -65°C. varied with the pressure of vapour used but the average value obtained was 162. (M.W. of $(PNF_2)_3$ = 248.9). When more of the less volatile component was added the 'molecular weight' increased. The bands in the infra-red spectrum that were not due to $(PNF_2)_3$ were identical with those due to benzene; the ^1H nuclear magnetic

resonance spectrum of all the volatile material consisted of a single sharp peak at 2.74 τ (lit. pure C_6H_6 has a single peak at 2.63τ). The small difference in the chemical shift probably arises from the effect on the protons of the $(PNF_2)_3$ molecules which were in a large excess. From the white involatile residue, soxhlet extraction with benzene for 12 hours yielded a white solid (0.95g.) m.p. 225°C. (lit. $(C_6H_5)_4Sn$ m.p. 224°C.). Soxhlet extraction of the residue insoluble in benzene with methanol, for 18 hours, yielded a white solid (24mg.) which decomposed above 350°C. The X-ray powder photograph of this was identical with that of $(C_6H_5)_3SnF$.

Pentafluorosulphur Chloride

Tetraphenyltin (3.0g.) was allowed to react with excess SF_5Cl at 110°C. for 30 hours. The volatile product, a pale yellow solid, was condensed at -196°C. This yielded a fraction volatile at -78°C., a colourless gas at room temperature. The infra-red spectrum of this fraction showed no bands due to SF_5Cl but a series of strong, complex bands in the region 1660-1000cm^{-1} with strong bands at 847 and 722cm^{-1}. There was no C-H absorption in the spectrum. From the extreme volatility of the fraction and its infra-red spectrum, it was concluded that a mixture of fluorocarbons was present. The other volatile product proved to be a yellow liquid. This compound fumed in moist air and attacked

grease, so an accurate molecular weight could not be obtained; the value obtained was 194. The infra-red spectrum showed the following peaks:- 1653(m), 1181(vs), 1111(vs), 755(m). The ^{19}F nuclear magnetic resonance spectrum of the liquid consisted of two single peaks in the ratio 3:1 at +17.8 and +20.0ppm. from benzotrifluoride respectively. As the peaks showed no fine structure it is likely that the signals arise either from ^{19}F nuclei in different compounds or from widely separated nuclei in the same compound. Meaningful analytical data could not be obtained.

The involatile residue from the reaction was black. Soxhlet extraction of this with benzene for 15 hours gave a dark red solution, from which a yellow solid (0.49g.) m.p. 116°C. was isolated (lit. rhombic sulphur m.p. 112.8°C., monoclinic 118.75°C.). This showed no vibration in the infra-red region and elemental tests were positive only for sulphur. The other product from the red solution was a light brown solid. An X-ray powder photograph showed this to be crystalline but was characteristic of neither $(C_6H_5)_3SnF$ nor $(C_6H_5)_4Sn$. Extraction of the residue with ethanol gave a dark brown tar. The residue after extraction proved to be carbon.

Arsenic pentafluoride

Tetraphenyltin (1.9g.) was allowed to react with

AsF_5 (ca 3g., containing some $AsOF_3$) at 120°C. for 18 hours. The products volatile at room temperature condensed to a white solid at -196°C. The fraction volatile at -80°C. showed bands due to $AsOF_3$ in its infra-red spectrum (MITRA 1958), the As-F vibration characteristic of AsF_5 was very weak. The other volatile compound was a colourless liquid (ca 1.5ml.) of molecular weight 133 (AsF_3 M.W. = 131.9). Its infra-red spectrum was identical with that of AsF_3 (AYNSELEY, DODD, LITTLE 1962). The non-volatile dark brown residue was extracted (soxhlet) with acetone for 6 hours. A dark brown solid was precipitated from this red solution by adding a large excess of petroleum ether. The infra-red spectrum of this was very complex although bands characteristic of aromatic C-H and C=C vibrations were observed. An X-ray powder photograph of the substance showed no lines.

Reactions with Tetrakis(pentafluorophenyl)tin

Sulphur tetrafluoride

$(C_6F_5)_4Sn$ (1.1g.) and SF_4 (containing some SOF_2) were allowed to react at 130°C. for 22 hours. A pink volatile solid was condensed at -196°C. after the reaction. Fractionation of this yielded a fraction volatile at -78°C whose infra-red spectrum showed bands characteristic of SF_4 and SOF_2. The other volatile

product was a pink liquid (ca 2ml.) that attacked mercury. The gas infra-red spectrum of this showed bands characteristic of a C_6F_5- group (BIRCHALL, HASZELDINE 1959). Its ^{19}F nuclear magnetic resonance spectrum was characteristic of a C_6F_5X compound (see Ch.3). The colour of the compound did not change even on very slow distillation at -65°C. No adduct was formed with BF_3. Analysis of the compound gave C - 32.48, F - 39.82, difference from 100% - 27.04; $(C_6F_5)_2Sn$ requires C - 31.83, F - 41.97, Sn - 26.22. Analysis for sulphur gave S - 0.66. No S-F bands were observed in the infra-red spectrum nor was any S-F signal observed in the N.M.R. spectrum, so it was concluded that the sulphur was present as an impurity.

Sublimation of the white residue was carried out and at 150°C. a very small amount of a white compound sublimed. This had m.p. 216°C. (lit. $(C_6F_5)_4Sn$ m.p. 215°C. subl. 150°C. in vacuo). The white residue (0.34g.) was almost insoluble in every solvent tried. Its infra-red spectrum was characteristic of a C_6F_5- group. Analysis gave C - 33.21, F - 47.10, Sn - 19.39; $(C_6F_5)_3SnF$ requires C - 33.83, F - 47.58, Sn - 18.58. The compound was stable thermally, decomposing at 300°C. Refluxing the compound with ethanolic potash for several hours had no effect, $(C_6F_5)_3SnF$ being recovered

unchanged. The reaction was repeated using the same conditions. A yellow liquid was isolated whose gas infra-red spectrum was identical with that of the red liquid. $(C_6F_5)_3SnF$ was the other product. On exposing the liquid to moist air it fumed and the yellow colour was discharged. A liquid film infra-red spectrum of the colourless oil formed was similar to that of the yellow liquid taken in the gas phase.

The reaction was repeated using a greater excess of SF_4 (ca 4g. SF_4 to 0.8g. $(C_6F_5)_4Sn$). The SF_4 was purified by making the BF_3 complex. A small fraction of the product was volatile at -78°C., an infra-red spectrum showed this to be SF_4. The fraction involatile at -78°C. was a colourless liquid (ca 0.5ml.), the infra-red spectrum of which contained a complex set of bands in the region 900-1700cm^{-1} but was not the same as the previous product. A constant value could not be obtained for the molecular weight, but the average value was 134.

The residue in the bomb was a grey solid from which nothing could be sublimed. Soxhlet extraction of this with acetone for 12 hours, gave a deep red solution, from which a dark brown solid was crystallised (0.1g.), decomp. 320°C. Its infra-red spectrum was identical with that of $(C_6F_5)_3SnF$. The black residue after acetone extraction (0.4g.) proved to be carbon.

Boron trifluoride

There was no reaction between $(C_6F_5)_4Sn$ and BF_3 when they were heated to 130°C. for 65 hours.

Phosphorus pentafluoride

$(C_6F_5)_4Sn$ (1.5g.) was reacted with excess PF_5 at 140°C. for 6 days. The fraction volatile at -78°C. was shown to be PF_5 from its infra-red spectrum. The other volatile product (100mg.) was a colourless liquid. The infra-red spectrum of this was identical with that obtained from the reaction with SF_4 in which decomposition took place. The 'molecular weight' of this fraction was not constant. The average value obtained was 153. The ^{19}F nuclear magnetic resonance spectrum of the compound dissolved in benzene showed three sets of complex peaks but little could be deduced from them. A white solid (0.8g.) was sublimed from the residue at 150°C. leaving a small quantity of grey solid. The infra-red spectrum of the latter was identical with that of $(C_6F_5)_3SnF$.

Reactions of Sulphur Tetrafluoride with Tetralkyltins

Tetra-n-butyltin

$(C_4H_9)_4Sn$ (10.6g.) and SF_4 (ca 5g.) were allowed to react at 20°C. for 12 hours. The volatile products were collected and fractionated. An infra-red spectrum of the fraction volatile at -116°C. showed bands due to SF_4 and also bands at 2967, 2899(sh) and 1028cm^{-1}.

The fraction involatile at -116°C. was a colourless liquid, molecular weight 86.4. Its infra-red spectrum showed bands due to C-H, C-C and C-F(?) vibrations. The proton magnetic resonance spectrum of the compound consisted of three sets of complex peaks at 6.02, 7.79 and 8.59↑. The infra-red spectrum of the liquid residue consisted of bands characteristic of an alkyl group.

Tetra-n-propyltin

$(C_3H_7)_4Sn$ (6.7g.) and SF_4 (ca 5g.) were allowed to react at 20°C. for 12 hours. The volatile products were similar to those from the $(C_4H_9)_4Sn$ reaction. From the liquid residue a white solid was extracted with methanol. The infra-red spectrum of this compound showed bands characteristic of an alkyl group. It decomposed above 350°C. Three sets of analyses were obtained from the same sample, as follows:-

C	H
28.66	6.03
28.48	5.95
33.04	5.44

$(C_3H_7)_2SnF_2$ requires C - 29.67, H - 5.77.

This reaction was repeated, sealing the reactants in a Carius tube. At -180°C. an orange solid was formed; on warming to room temperature the colour faded and a white

solid was precipitated from the yellow solution. On leaving the reaction mixture at 20°C. for several days the solution darkened and a black solid was precipitated. This was not investigated further.

CHAPTER TWO

THE REACTIONS OF BIS(TRIFLUOROMETHYL)PEROXIDE WITH SOME METAL CARBONYLS

Introduction

This work was carried out in an attempt to prepare trifluoromethoxy derivatives of transition metal carbonyls, which are unknown. Alkoxy derivatives of metal carbonyls have not been reported although many metals form alkoxides (BRADLEY 1960). All metal carbonyl compounds containing sigma fluorocarbon groups reported so far, have a metal-carbon bond linking the polyfluoro group to the transition metal.

Polyfluoroaliphatic and Aromatic Derivatives

Perfluoroalkyl metal carbonyl compounds have been prepared by decarbonylation of the corresponding fluoroacyl metal carbonyl (KAESZ, KING, STONE 1960). This is effected by heating the compound. Fluoroacyl metal carbonyls are prepared by reaction of a perfluoroacid chloride with the sodium salt of the carbonyl. The reaction scheme for this preparation of perfluoroalkyl metal carbonyls is:

$$xR_fCOCl + Na_xM(CO)_{6-x} = (R_fCO)_xM(CO)_{6-x} + xNaCl$$

$$(R_fCO)_xM(CO)_{6-x} \xrightarrow{heat} (R_f)_xM(CO)_{6-x} + xCO$$

Compounds such as $CF_3Mn(CO)_5$ and $C_2F_5Re(CO)_5$ have been prepared using this method. In some cases the perfluoroacyl compound is unstable and decarbonylates spontaneously; e.g. $(CF_3)_2Fe(CO)_4$ is prepared directly from the reaction of $Na_2Fe(CO)_4$ and CF_3COCl. This type of reaction has been found to be quite general (KING, PITCHER, STAFFORD, TREICHEL, STONE 1961). Manganese pentacarbonyl hydride adds across the double bond in perfluoroölefines to give fluorocarbon manganese pentacarbonyl derivatives (TREICHEL, PITCHER, STONE 1962). $(\pi\text{-}C_5H_5)W(CO)_3H$ also does this (TREICHEL, MORRIS, STONE 1963). When an unsymmetrical olefine is used, the direction in which addition takes place depends on the reaction conditions. (WILFORD, TREICHEL, STONE 1963). When the reaction is irradiated with ultra-violet light a mixture of isomers results, the main product being the opposite to that obtained without ultra-violet radiation. It is thought that addition can proceed in two ways, either by a free radical mechanism or by a four centre mechanism. The former is favoured by ultra-violet light and by low pressures. All these compounds are stable to light and moisture and in most cases their thermal stability is good.

Pentafluorophenyl metal carbonyls of manganese have recently been reported. They are easily prepared by the reaction of either C_6F_5Li (TREICHEL, CHAUDHARI, STONE 1963) or C_6F_5MgBr (RAUSCH 1964) with pentacarbonyl manganese bromide. $(\pi\text{-}C_5H_5)Fe(CO)_2(C_6F_5)$ and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ have been prepared by similar methods. These compounds are stable, similar to perfluoroalkyl compounds.

Trifluoromethyl Derivatives of Oxygen

The chemistry of compounds containing the CF_3O- group is not extensive. Fluorine in the α position to an hydroxyl group is unstable, due to the great stability and volatility of CHF_3 and such compounds are unknown. The only fluorine containing primary alcohols known are those where fluorine occupies the β position, secondary and tertiary alcohols and glycols are also known (LOVELACE, RAUSCH, POSTELNEK 1958).

In contrast to the hydrocarbon series, trifluoromethyl hypofluorite is stable. It can be prepared by the reaction of fluorine with methyl alcohol or carbon monoxide over an AgF_2 catalyst (KELLOGG, CADY 1948). CF_3OF readily liberates iodine and bromine from solutions of their salts, COF_2 being the other product and will react with molten NaCl to liberate chlorine. It also liberates oxygen from solutions containing OH^- ion.

CF_3OF is a strong fluorinating agent, giving Hg_2F_2, LiF, and SF_4 at room temperature with Hg, Li and S respectively (PORTER, CADY 1951). The other product from the reaction is COF_2.

The thermal decomposition of CF_3OF proceeds reversibly between 367° and 467°C. the equilibrium being $CF_3OF \rightleftharpoons COF_2 + F_2$. However at temperatures between 250° and 300°C. it reacts with carbonyl fluoride to give bis (trifluoromethyl)peroxide. The preparation of this compound was originally described by SWARTS (1933) who prepared small quantities by the electrolysis of solutions containing the trifluoroacetate ion. CF_3OOCF_3 is most conveniently prepared by the reaction of carbon monoxide with fluorine in a 2:1 volume ratio over an AgF_2 catalyst at 180°C. (PORTER, CADY 1957). It is a stable, non-explosive gas (b.p. -37°C.) which decomposes about 225°C. giving COF_2. It slowly liberates iodine from KI solution, the equation being $CF_3OOCF_3 + 2I^- + 2H_2O = I_2 + 2CO_2 + 4HF + 2F^-$.

Bis(monofluorocarbonyl)peroxide has recently been prepared by the reaction of a mixture of fluorine, carbon monoxide and excess oxygen (ARVIA, AYMONINO, SCHUMACHER 1962). This is an oxidising agent, liberating I_2 from KI and O_2 from solutions containing OH^- ions.

Perfluoroalkyl ethers are inert compounds, more

stable than the corresponding hydrocarbon compounds. They are cleaved only when heated with $AlCl_3$ (TIERS 1955).

Trifluoromethoxy-derivatives of organic compounds have been described, using CF_3OF to introduce the CF_3O- group. CF_3OF adds quantitatively across ethylene in the presence of ultra-violet light to give $CF_3OCH_2CH_2F$ (ALLISON, CADY 1959). Analogous reactions take place with cyclopropane and benzene, giving $CF_3OCH_2CH_2CH_2F$ and a mixture of $PhOCF_3$ and PhF respectively. These reactions are sensitive to the reaction conditions; oxidation to carbon can take place very easily if more vigorous conditions are used.

Reactions with Metal Carbonyls

Dimanganese decacarbonyl

This was thought to be a suitable carbonyl to use as the Mn-Mn bond would be broken easily. CF_3OOCF_3 reacts with SF_5OOSF_5 to give a mixed peroxide, CF_3OOSF_5 (MERILL, CADY 1963). This reaction does not occur in the absence of ultra-violet light and probably involves the formation of $SF_5O\cdot$ radicals as the initiating step in the reaction. CF_3OOCF_3 has been reported to form $CF_3O\cdot$ radicals when irradiated with ultra-violet light or when heated to 90°C. (ROBERTS 1962). In the present work the reaction of CF_3OOCF_3 with $Mn_2(CO)_{10}$ at 90°C. produced CO, COF_2 and a flesh pink inorganic solid which was

presumed to be manganous fluoride. Irradiation of $Mn_2(CO)_{10}$ and CF_3OOCF_3 in a Carius tube gave COF_2, CO and SiF_4 as gaseous products. A volatile purple solid isolated had peaks in the C-F region of the infra-red but could not be characterised. The intense colour of the compound is characteristic of Mn(VII) compounds. The volatility is also characteristic of a high oxidation state of the metal. Once again a flesh pink non-volatile residue was the other product.

When a mixture of $Mn_2(CO)_{10}$ and CF_3OOCF_3 was shaken together in an inert solvent at 24°C. the volatile products were CO and COF_2. An unstable orange solid sublimed from the reaction residue had three absorption bands in the C=O stretching region at 2066, 2037 and 2000cm^{-1} and a broad absorption (in the C-F region) with maxima at 1034, 1075 and 1124(sh)cm^{-1}. Analysis data together with infra-red evidence suggest that the compound is $Mn(CO)_5OCF_3$ but are not conclusive. From the presence of the SiF_6^{2-} ion in the non-volatile residue and from the fact that no reaction took place in a steel bomb under similar conditions, it is likely that a reaction on the glass in the presence of ultra-violet radiation is concerned in the reaction mechanism.

<u>π-Dicyclopentadienyldiiron tetracarbonyl</u>

The reaction of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ with CF_3OOCF_3

at 24°C. gave a dark brown solid similar in appearance to the starting material. Its infra-red spectrum showed that there were no bridging carbonyl groups in the product. The peaks in the terminal C=O region were as follows: 2320(vw), 2110(m), 2075(vs), 2037(vs), 1838(w)cm^{-1}. These peaks were recorded from a methylene chloride solution spectrum. A broad absorption band in the 8-10μ region (nujol mull) showed peaks as follows: 1193(sh), 1140(s), 1064(s), 1033(sh)cm^{-1}. This compound was very unstable and could not be characterised.

The evidence obtained indicates that the metal-metal and the bridging carbonyl bonds are broken in the reaction. From the absence of any volatile products it appears that a smooth reaction takes place.

Iron pentacarbonyl

The reaction between $Fe(CO)_5$ and CF_3OOCF_3 was very vigorous, reaction being complete after 30 minutes at -30°C. The volatile product was COF_2; no evidence for the presence of fluorocarbon iron carbonyl compounds in the residue was found. It appeared to contain $Fe(CO)_5$ and an inorganic solid.

Chromium hexacarbonyl

The products from the reaction of $Cr(CO)_6$ with CF_3OOCF_3 at 120°C. were a mixture of CO, COF_2 and unreacted CF_3OOCF_3 and chromic fluoride. No evidence

for a fluorocarbon carbonyl compound was found.

Molybdenum hexacarbonyl, sodium fluoride mixture

A 1:2 molar ratio mixture of $Mo(CO)_6$ and NaF was allowed to react with CF_3OOCF_3 at 220°C. The volatile product was COF_2 and the other product a pale brown solid which hydrolysed in water giving a red solution. Analysis indicated that this was Na_2MoF_6.

Molybdenum hexacarbonyl

It was thought that the ultra-violet irradiation of a mixture of $Mo(CO)_6$ and CF_3OOCF_3 might produce replacement of CO by CF_3O- analogous to the reactions of acetonitrile (STRÖHMEIER, SCHÖNAUER 1961) and acrylonitrile (MASSEY 1962) with $Mo(CO)_6$ and $W(CO)_6$. It has been reported that this type of reaction involves the $M(CO)_5$· radical as the initiating species (DOBSON, AMR EL SAYED, STOLZ, SHELINE 1962). However irradiation was unsatisfactory, a dark brown inorganic solid being produced in low yield. The volatile products were CO and COF_2.

The reaction of $Mo(CO)_6$ with CF_3OOCF_3 at 90°C. gave CO and COF_2 as volatile products. A few mg. of a white compound were also isolated, this was volatile at room temperature and had a strong band at 2031cm^{-1} characteristic of a CO absorption. Not enough of the compound was obtained for analysis however. The residue from the reaction was a light brown solid which was very

easily hydrolysed. The infra-red spectrum of the compound (nujol mull) showed three peaks in the C=O region at 2188(m), 2092(vs) and 2008(m). There were also broad strong peaks at 1032 and 556cm^{-1}. The compound could not be characterised further.

Tungsten hexacarbonyl

The volatile products from the reaction of $W(CO)_6$ with CF_3OOCF_3 were CO, COF_2 and WF_6. The involatile product was a pale green solid which was unstable to moist air and to heat. This could not be characterised.

Discussion of the Reactions

Very little evidence for the introduction of CF_3O° groups into carbonyl compounds was found in these reactions. The main reaction of CF_3OOCF_3 is that of a fluorinating agent i.e. $CF_3OOCF_3 = 2COF_2 + 2F$. This process could take place by the dissociation of CF_3OOCF_3 to give COF_2 and CF_3OF and subsequent fluorination of the carbonyl by the latter. Alternatively CF_3O° radicals could be formed, these being unstable with respect to COF_2 would breakdown and fluorination would result. An analogous reaction has been reported between fluoroazoalkanes and metal carbonyls (CHAMBERS, TULLOCK, COFFMAN 1962). The overall reaction is a defluorination of the perfluoroazoalkane to give a bis(fluoroalkylidene)azine.

i.e. $R_FCF_2N{=}NCF_2R_F + M(CO)_x{=}R_FCF{=}N{-}N{=}CFR_F + MF_2{+}xCO$.

The fluorination of a $Mo(CO)_6$,NaF mixture with CF_3OOCF_3 gives a Mo(IV) complex fluoride in contrast to SF_4 which gives a Mo(V) complex (KEMMITT, SHARP 1961).

In the cases where other reactions besides fluorination occurred, the products were too unstable to be characterised properly. However, some information can be obtained from their infra-red spectra.

The metal-carbon bond in metal carbonyls has been described in terms of a synergic interaction between the donation of the carbon lone pair of electrons to a vacant metal orbital and the back-donation of electrons from a filled metal d orbital to low lying π anti-bonding orbitals of CO (ORGEL 1960). The consequence of electrons occupying a π antibonding orbital of CO is a reduction of the order of the CO bond and a lowering of the C=O terminal stretching frequency. This is particularly noticeable when electron donating ligands are introduced (CHATT, PAUSON, VENANZI 1960). In carbonyl compounds containing highly electronegative substituents the degree of π back donation is reduced, due to the attraction of the electrons by the electronegative substituents. Thus an increase in CO stretching frequency, from that of the unsubstituted carbonyl, results. This has been observed for perfluoroalkyl carbonyls (PITCHER, STONE 1962),

perfluoroaryl carbonyls (TREICHEL, MORRIS, STONE 1963) and metal carbonyl fluorides (RUSSELL 1963).

A shift of CO absorption to higher frequency occurs in the products from the reactions with $Mn_2(CO)_{10}$, $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ and $Mo(CO)_6$ indicating the presence of a highly electronegative group. In the latter two cases the number of bands changes, indicating a change in the symmetry of the molecule (ORGEL 1962). However, the spectrum of the $Mo(CO)_6$ product was taken in a nujol mull, this precluding any comment about the symmetry of the product. The extreme sensitivity of the products, from the $Mo(CO)_6$ and $W(CO)_6$ reactions, to water and their reaction with glass on heating, to give SiF_4, are characteristic of Mo and W fluorides. The band at $556cm^{-1}$ in the infra-red spectrum of the $Mo(CO)_6$ product could be due to a Mo-F vibration. More work is required to characterise the products from these reactions. Previous attempts to prepare carbonyl fluorides of Mo and W by reaction of the carbonyls with fluorine or binary fluorides have failed. With $Mo(CO)_6$ the products are MoF_5 and MoF_4 (PEACOCK 1957; HARGREAVES, PEACOCK 1960) and with $W(CO)_6$, WF_6 is the product (HARGREAVES, PEACOCK 1958 and 1960). The existence of an unstable carbonyl complex of MoF_5 has been suggested (RUSSELL 1963).

Conclusion - Bis(trifluoromethyl)peroxide generally

behaves as a fluorinating agent in the presence of metal carbonyls. Trifluoromethoxy derivatives of metal carbonyls seem to be very unstable but where evidence exists for the formation of such compounds, the reaction is complex. The products obtained from these reactions are sensitive to the reaction conditions used.

EXPERIMENTAL

The reactions were carried out in a stainless steel bomb (as already described) or in Carius tubes. Carbonyls (obtained from Ethyl Co. Ltd. and Molybdenum Climax Co. Ltd.) were resublimed before use and the reaction vessel charged in the dry box. Strict precautions were taken to ensure anhydrous conditions during the reaction. Bis(trifluoromethyl)peroxide, (a gift from Imperial Chemical Industries Ltd., Alkali Division), was stored in a cylinder that could be connected to the vacuum line. A suitable quantity was distilled out on to NaF and redistilled at -78°C. before use. An infra-red spectrum of the gas was identical with that reported by PORTER and CADY (1957). Usually an excess of CF_3OOCF_3 was used in the reaction, this providing an autogenous pressure and also acting as a solvent.

A gas infra-red spectrum of the volatile products gave valuable information as to their nature. The C-F

vibrations in the region 1200-1300cm^{-1} in CF_3OOCF_3 are easily recognised, as is the presence of carbonyl fluoride, which has a C=O vibration at 1944cm^{-1} and C-F vibrations at 1249 and 965cm^{-1}. (NIELSEN, BURKE, WOLTZ, JONES 1952). Carbon monoxide absorbs at 2186cm^{-1} (LAGEMANN, DICKLEY 1947).

Reactions with Metal Carbonyls

Manganese carbonyl

$Mn_2(CO)_{10}$ (0.4g.) was heated with excess CF_3OOCF_3 (ca 3ml. liquid) at 90°C. for 18 hours in a bomb. From an infra-red spectrum of the volatile products condensed at -196°C. COF_2 and CF_3OOCF_3 were identified. The molecular weight of the product was 71 (average) (CF_3OOCF_3, M.W.=170; COF_2, M.W.=66). The flesh-pink residue showed no C-F nor C=O bands in the infra-red and was presumed to be manganous fluoride.

A mixture of $Mn_2(CO)_{10}$ (0.33g.) and CF_3OOCF_3 (2ml.) were irradiated (ultra-violet) for 6 hours in a Carius tube using an 'Hanrovia' mercury lamp. $Mn_2(CO)_{10}$ was soluble in CF_3OOCF_3 to give a yellow solution. The product condensed at -196°C. and volatile at -78°C. had an infra-red spectrum containing bands characteristic of COF_2, CF_3OOCF_3 and SiF_4. The 'molecular weight' of the fraction was 78. In addition some uncondensable gas (presumed to be CO) was collected. The other volatile product was

a dark purple solid (20mg.) (V.P. ~3mm. at 20°C.). A gas infra-red spectrum of this showed bands at 1030 and 1280cm^{-1}. This compound was rapidly decomposed in moist air but gave a purple solution in CCl_4. An infra-red spectrum of the solution showed three strong bands at 1260, 1100 and 1015cm^{-1}. When a solution of triphenyl-phosphine in CCl_4 was added, the solution turned yellow and a white precipitate was formed, but this was decomposed when recrystallisation was attempted. The residue in the tube was flesh-pink and showed no absorption in the infra-red. Irradiation was attempted under different conditions in an attempt to increase the yield of the purple solid but this was unsuccessful.

$Mn_2(CO)_{10}$ (0.63g.) was allowed to react with CF_3OOCF_3 (ca 3ml.), using Arcton 113 ($CCl_2F\cdot CClF_2$) as solvent. The reaction was carried out in a Carius tube at 24°C. for 12 hours. The volatile product, condensed at -196°C. had an infra-red spectrum with bands characteristic of COF_2 and CF_3OOCF_3. Arcton 113 was removed from the reaction mixture at -30°C. under vacuum, leaving an orange solid; this was sublimed at 60°C. An infra-red spectrum (nujol mull) showed three sharp absorptions in the C=O stretching region and a broad absorption band in the region 1000-1100cm^{-1}. This solid was very unstable, decomposing within minutes in moist air and so was handled

under dry N_2 or in the dry box. Analysis, found C - 26.79; required for $Mn(CO)_5OCF_3$ C - 25.71. The residue showed a peak characteristic of the SiF_6^{2-} ion. No reaction occurred in a steel bomb.

π-Dicyclopentadienyldiion tetracarbonyl

π-$Cp_2Fe_2(CO)_4$ was prepared by the method of PIPER, COTTON and WILKINSON (1955) and was reacted at 24°C. for 12 hours with excess CF_3OOCF_3 and Arcton 113 in a Carius tube. The product volatile at -78°C. had an infra-red spectrum characteristic of CF_3OOCF_3. After removal of Arcton 113 a dark brown solid remained. The infra-red spectra of this solid showed a C-H vibration and peaks in the terminal C=O region but no peak in the bridging C=O region. In addition there was a broad set of peaks in the region 1200-1000cm^{-1}. No satisfactory analyses could be obtained for this compound.

Iron pentacarbonyl

$Fe(CO)_5$ (excess) was allowed to react with CF_3OOCF_3 in a Carius tube at -30°C. for ½ hour. A vigorous reaction took place, a white solid appearing on the side of the tube. Examination of the volatile products yielded a non-condensable gas and a fraction volatile at -78°C. The infra-red spectrum of the latter was identical with that of COF_2; its molecular weight was 63.4 (M.W. of COF_2=66.0). The non-volatile residue consisted

of a white solid and a dark brown tar which spontaneously inflamed when the tube was opened in the dry box. The white solid showed no absorption in the region 4000-650cm^{-1} and was presumed to be inorganic. Its colour rapidly changed to dark brown on exposure to moist air. An infra-red spectrum of the brown tar showed it to contain $Fe(CO)_5$.

Chromium hexacarbonyl

$Cr(CO)_6$ (0.54g.) was allowed to react with CF_3OOCF_3 (ca 3ml.) for 22 hours at 120°C. The volatile products were a non-condensable gas and a fraction condensed at -196°C. whose infra-red spectrum showed bands characteristic of COF_2 and CF_3OOCF_3. The non-volatile residue had no absorption in the region 4000-650cm^{-1}. Analysis, Cr found 46.1; required for CrF_3, Cr - 47.7

Molybdenum carbonyl, sodium fluoride mixture

A mixture of $Mo(CO)_6$ (0.69g.) and NaF (0.21g.) in a ratio 1:2 was reacted with CF_3OOCF_3 (ca 3ml.) at 220°C. for 24 hours. The volatile products consisted of a non-condensable gas and a fraction condensed at -196°C. The molecular weight of the compound was 61.4 (M.W. of COF_2=66) and its infra-red spectrum was identical with that of COF_2. The involatile product was a light brown solid, showing no absorption in the region 4000-650cm^{-1} and hydrolysing to give a red solution. Analysis found

Mo = 39.6; required for Na_2MoF_6, Mo = 37.5.

Molybdenum hexacarbonyl

$Mo(CO)_6$ (0.83g.) and CF_3OOCF_3 (ca 3ml.) were irradiated with ultra-violet light for 10 hours in a Carius tube. The volatile products were a non-condensable gas and a fraction condensed at -196°C. An infra-red spectrum of this showed it to be a mixture of COF_2 and CF_3OOCF_3. From the residue 0.37g. of $Mo(CO)_6$ were recovered by sublimation, leaving a dark brown solid (0.01g.) that appeared to be stable in moist air and showed no absorption in the 4000-650cm^{-1} region.

$Mo(CO)_6$ (0.88g.) and CF_3OOCF_3 (ca 3ml.) were allowed to react for 18 hours in a bomb at 90°C. The most volatile products were a mixture of CO, COF_2 and CF_3OOCF_3 (identified by their infra-red spectra). The other volatile product was a white solid (ca 5mg.) that had a vapour pressure of 7mm. at 24°C. The gas infra-red spectrum of this compound showed bands at 2031(vs), 1284(m), 1031(s), 794(w) and 720(s). After unreacted $Mo(CO)_6$ had been sublimed from the non-volatile residue, a light brown solid remained. This was very unstable, some decomposition taking place in the dry box. In moist air the solid fumed and the following colour changes were noted: light-brown → red-brown → dark-brown. In water hydrolysis occurred giving a red solution. The infra-

red spectrum (Nujol mull) showed three bands in the terminal C=O stretching region, a broad peak at 1032cm^{-1} and one at 556cm^{-1}. Analysis, found Mo - 31.2. No satisfactory C and F analyses were obtained for this compound. When a sample of the compound was heated to 180°C, carbon monoxide and SiF_4 were evolved (identified by their infra-red spectra). The residue was a dark brown solid similar to that obtained from the irradiation experiment.

Tungsten hexacarbonyl

$W(CO)_6$ (0.5g.) and CF_3OOCF_3 (ca 3ml.) were allowed to react together at 110°C. for 18 hours in a bomb. The products were a non-condensable gas, the infra-red spectrum of which was characteristic of CO and a fraction condensed at -196°C. and volatile at -78°C. The 'molecular weight' of this fraction was 72.5 (average) (M.W. of COF_2=66; M.W. of CF_3OOCF_3=170). An infra-red spectrum showed bands characteristic of COF_2 and CF_3OOCF_3. The fraction involatile at -78°C. (46mg.) had a molecular weight of 286 (M.W. of WF_6=297.9) and its infra-red spectrum was consistent with that of WF_6 (BURKE, SMITH, NIELSEN 1952). No $W(CO)_6$ was recovered by sublimation from the pale green involatile residue, which was very unstable, fuming in the dry box. The solid hydrolysed readily to give a dark-green solution from which a green

solid precipitated. On heating the compound to 100°C. in vacuum, a non-condensable gas was evolved together with a small quantity of SiF_4 (identified by its infra-red spectrum). When the reaction was carried out at higher temperatures a brown tar was obtained instead of the green solid.

CHAPTER THREE

THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME FLUOROBENZENE DERIVATIVES

Introduction

Nuclear magnetic resonance (N.M.R.) spectroscopy is now well established as a chemical tool both for structure determination and to obtain information about the chemical bond. Since the first detection of nuclear resonance effects in bulk matter (PURCELL, TORREY, POUND 1946; BLOCH, HANSEN, PACKARD 1946) there have been many experimental and theoretical advances in the fields of broad line and high-resolution N.M.R. spectroscopy.

Although most high resolution work has been done with hydrogen containing compounds, fluorine compounds occupy an important position in the field. The ^{19}F isotope (100% abundance) has a spin of $\frac{1}{2}$, gives rise to strong signals and has a favourable spin-lattice relaxation time (T_1). In addition fluorine forms many ionic and covalent compounds which are suitable for study by this technique.

Chemical Shifts

The ~~chemical shift~~ shielding of a nucleus is defined as the

difference between the magnetic field 'seen' by the nucleus and the applied magnetic field. The theory of chemical shifts (due to RAMSEY 1950) states that they result from diamagnetic and paramagnetic contributions. For protons, chemical shifts are almost entirely due to the diamagnetic contribution (Lamb term) arising from the magnetic field opposing the applied field set up by the extranuclear electrons. Paramagnetic terms can be important in proton chemical shifts where a ring current is involved (POPLE 1956) e.g. in aromatic compounds.

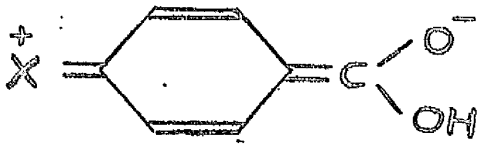
The chemical shifts found in fluorine compounds are an order of magnitude greater than those in the corresponding hydrogen compounds and are too great to be accounted for by variations in the Lamb term. SAIKA and SLICHTER (1954) have devloped a quantitative theory of ^{19}F shielding based on contributions from the paramagnetic term. These arise from local magnetic fields set up by orbital motions of the 2p electrons, as a result of unequal electron population of the $2p_x$, $2p_y$ and $2p_z$ orbitals. The paramagnetic contribution is zero in the spherically symmetrical F^- ion and leads to a negative contribution to the shielding constant for a covalently bonded F atom, as the orbital field is in the same direction as the applied field. This theory has been successful in explaining quantitatively the chemical

shift of HF relative to F_2. Experimentally it has been found that the shielding of ^{19}F nuclei in a series of binary M-F compounds decreases with increasing covalent character of the M-F bond (GUTOWSKY, HOFFMAN 1951). However, additional factors can operate to destroy this simple concept (e.g. MEYER, GUTOWSKY 1953).

^{19}F Shielding in Fluoroaromatics

^{19}F chemical shifts have been studied in a large number of substituted fluorobenzenes. GUTOWSKY, McCALL, McGARVEY and MEYER (1952) obtained fairly precise linear correlations between the chemical shifts of meta and para substituted fluorobenzenes (relative to fluorobenzene) and the Hammett sigma (σ) function of the substituent. The sigma function is a measure of the electron attracting or withdrawing power of the substituent and is defined by $\sigma = \log_e \frac{K}{K_o}$, where K and K_o are the dissociation constants of the substituted and unsubstituted benzoic acid in water at 25°C. (HAMMETT 1935). More precise equations were obtained by TAFT (1957) who correlated shielding parameters with the separated Hammett inductive (σ_I) and resonance (σ_R) functions. These are defined by the relationship $\sigma = \sigma_I + \sigma_R$. The electronic effect of a substituent can thus be separated into its inductive effect through the sigma-bond system (σ_I) and its resonance or mesomeric effect through the pi- system (σ_R).

The σ_I values were obtained by measuring acid dissociation constants of saturated 'pseudo benzene' molecules i.e. 4-substituted bicyclo-2,2,2-octane-1-carboxylic acids (ROBERTS, CLEMENT, DRYSDALE 1951). A better correlation is obtained for para substituted fluorobenzenes if σ_R^o values of the substituent are used (TAFT, EHRENSON, LEWIS, GLICK 1959). These values are obtained by compensating for conjugation with, and/or strong polarisation of the centre by, the reaction centre. The difference $\sigma_R - \sigma_R^o$ is a measure of the contribution to the Hammett σ-value from the canonical form:



The dependence of ^{19}F shielding parameters of meta substituted fluorobenzenes on σ_I (TAFT, PRICE, FOX, LEWIS, ANDERSEN, DAVIS 1963a) and of para substituted fluorobenzenes upon σ_R^o (TAFT, PRICE, FOX, LEWIS, ANDERSEN, DAVIS 1963b), has been shown for a large number of substituents in different solvents.

This empirical treatment has been used by others to obtain new Hammett functions (BYSTROV, UTYANSKAYA, YAGUPOL'SKII 1961; SUHR 1964) and also to determine the electronic properties of substituents (MACIEL 1964).

The inductive and mesomeric effects of meta and para substituents can be transmitted to fluorine atoms two or three bonds removed from the aromatic ring (EATON, SHEPPARD 1963), as the chemical shifts of ^{19}F nuclei in substituted $ArOCF_3$, and $Ar-SF_5$ compounds can be correlated with σ_I or σ_R^0.

A theoretical treatment of ^{19}F shielding in fluorobenzenes has been given by KARPLUS and DAS (1961). An equation for the shielding relative to PhF has been derived, depending upon the change in ionic character and the change in double bond order of the fluorine bonding orbital.

The equation fits existing data for the chemical shifts of meta and para substituted polyfluorobenzenes but not for ortho substituents unless an empirical correction is applied.

An alternative treatment of ^{19}F shielding has been given by PROSSER and GOODMAN (1963). They treat the shielding (relative to PhF) as a function of the change in π-electron distribution throughout the molecule. The shielding equation obtained is a linear function of the change in π-electron charge density of the conjugating z F-orbital, the change in F-C π-electron bond order and the change in π-electron charge density of the bonding C atom. This equation has been found to

be valid for a number of para substituted fluorobenzenes (TAFT, PROSSER, GOODMAN, DAVIS 1963). In these compounds the change in π-charge density of the F atom (or of the C atom) is proportional to the change in C-F π-bond order, so the shielding is proportional to the change in F π-charge density. This treatment differs from that of KARPLUS and DAS in placing a higher dependence of the shift upon π-bond orders. However, an invarient sigma framework for the fluorobenzene was assumed in the calculations and an attempt to discover whether this is valid was inconclusive.

An empirical treatment of the ^{19}F chemical shifts in monofluoroaromatic compounds (DEWAR, FAHEY, GRISDALE 1963) using KARPLUS and DAS' equation indicates that the change in ionic character of the C-F bond is the most important factor in the shielding. Similar results have been obtained by other workers (IIO, INUKAI, ISOBE 1960).

The evidence as to which factor is most important in the shielding of ^{19}F nuclei in fluorobenzenes is conflicting but changes in both σ and π electron density of the F atom are involved. The effect of ortho substituents cannot be accounted for satisfactorily by any of these treatments. This ortho effect will be discussed later.

Electron Coupling of Nuclear Spins

The direct magnetic dipolar interactions between nuclei that are responsible for broadening N.M.R. absorption signals in the solid state (PAKE 1948) are effectively averaged out to zero in liquids, by the high frequency molecular rotations of the liquid state (BLOEMBERGEN, PURCELL, POUND 1948). It has been found that field independent fine structure superimposed on the chemical shift in the spectrum of a liquid, can be empirically described by an interaction energy $E_{NN'}$ between nuclear spin vectors $I_N I_{N'}$ of the form $E_{NN'} = hJ_{NN'} I_N \cdot I_{N'}$ (GUTOWSKY, McCALL 1951); where h is Planck's constant and $J_{NN'}$ is a constant characteristic of the molecule containing N and N' (the spin-spin coupling constant). A full theory based on the complete Hamiltonian for electron-nuclear interactions has been developed (RAMSEY, PURCELL 1952; RAMSEY 1953) but this requires a detailed knowledge of the electronic states of the molecule, particularly in the region near the nucleus, which makes the approximate wave-functions normally used for calculations inadequate. Both Molecular Orbital (McCONNELL 1956) and Valance Bond (KARPLUS, ANDERSON, FARRAR, GUTOWSKY 1957) approximations have been used to describe the interaction, in terms of coupling via electron spins and orbital motions.

Coupling between non-bonded protons is thought to occur mainly by a ~~(two electron)-(s-orbital)-(electron spin)~~ mechanism, known as the Fermi, or contact, interaction term. This operates only over relatively short bond distances, so proton coupling will be expected to decrease in magnitude when the number of bonds separating the nuclei increases, as is found experimentally.

Spin coupling involving ^{19}F nuclei is complicated by the ability of 'one electron orbital' and 'two electron spin and orbital' terms to make significant contributions to the coupling mechanism.

The absolute sign of a coupling constant depends upon the relative amounts contributed to the coupling mechanism from the terms already described; a positive value of J indicates that coupling of antiparallel nuclear spins produces a low energy state, for a negative J value the reverse is the case. Information about the relative signs of coupling constants can be obtained from some analyses of complex spectra (see later) and from double resonance experiments (MAHER, EVANS 1961; FREEMAN 1961). Such information is useful in determining the mechanisms of coupling in a given molecule.

Nuclear Spin-Spin Coupling in Aromatic Molecules:

^{1}H-^{1}H, ^{1}H-^{19}F and ^{19}F-^{19}F coupling constants have been determined in many fluorobenzenes. It has been

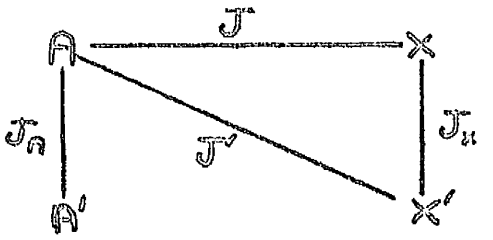
found (GUTOWSKY, HOLM, SAIKA, WILLIAMS 1957; RICHARDS, SCHAEFER 1958) that coupling constants are characteristic of the relative positions that the atoms occupy in the molecule. The following orders of magnitude are quite general: $J^{o}_{HH} > J^{m}_{HH} > J^{p}_{HH}$; $J^{o}_{HF} > J^{m}_{HF} > J^{p}_{HF}$ and $J^{o}_{FF} > J^{p}_{FF} > J^{m}_{FF}$. ^{19}F-^{19}F coupling constants are greater than the corresponding ^{1}H-^{1}H and ^{1}H-^{19}F values. For ^{1}H-^{1}H and ^{1}H-^{19}F coupling, the magnitude decreases with increasing number of bonds between the nuclei, consistent with the idea that coupling takes place by the Fermi contact mechanism. In the case of ^{19}F-^{19}F coupling other factors, possibly coupling through the π system, are involved.

A molecular orbital treatment of coupling in fluorobenzenes (WILLIAMS, GUTOWSKY 1959) enabled the magnitudes and signs of ^{1}H-^{1}H, ^{1}H-^{19}F and ^{19}F-^{19}F coupling constants to be calculated, reasonable agreement being obtained with experimental values. The signs of ^{1}H-^{1}H and ^{1}H-^{19}F coupling constants agree with those determined experimentally (BAK, SHOOLERY, WILLIAMS 1958). However, the relative signs of ^{19}F-^{19}F coupling constants that have been determined (EVANS 1962a) do not agree with those predicted. It is apparent that the approximations involved in calculating ^{19}F-^{19}F coupling constants lead to errors in the results.

General Features of the ^{19}F N.M.R. Spectra of Aromatic Compounds

The spectra of fluorine compounds are similar to those of the corresponding hydrocarbons, except that the chemical shifts and coupling constants are greater. Analysis of ^{19}F spectra is often easier than that of ^{1}H spectra as a spectrum can be treated as an $A_aM_mX_x\ldots\ldots$ system rather than an $A_aB_bC_c\ldots\ldots$ system.

In the present work it was often necessary to analyse spectra resulting from two pairs of equivalent nuclei. This system is designated A_2B_2 where the nuclei are strongly coupled compared to the chemical shift between them and A_2X_2 where the ratio of the coupling constant between A and B, to the chemical shift between A_2 and B_2 is small (<0.1). For ^{19}F spectra the latter was the case. The A_2X_2 system was first analysed by McCONNELL, McLEAN and REILLY (1955). Using group theoretical and angular momentum operators they factored the general four spin matrix to give explicit analytical expressions for the ~~twelve~~ twenty four transition frequencies and their intensities, using the following parameters: $K = J_A+J_{X'}$, $M = J_A-J_{X'}$, $N = J+J'$ and $L = J-J'$. The relationship between the nuclei and coupling constants is shown below.



The analysis of an A_2B_2 system proceeds in the same way except that explicit functions can be obtained for only six of the transitions. An A_2X_2 spectrum consists of two identical multiplets, each having ten lines symmetrical about the mid point of the multiplet. The effect of changing the values of K,M,L,N and the chemical shift between the nuclei, in A_2X_2 and A_2B_2 spectra has been discussed (GRANT, HIRST, GUTOWSKY 1963). Each multiplet of an A_2X_2 spectrum consists of a strong doublet, centred on the resonance frequency and of separation N and two symmetrical quartettes also centred on the resonance frequency. The assignment of the outer and inner lines of the quartettes depends upon the signs of K and M but the inner lines are always more intense.

From the spectral analysis it is possible to determine the magnitudes of N and L separately (and thus the relative signs of J and J') but it is not possible to distinguish between K and M, although their magnitudes can be determined. The final assignment of J and J' and of J_A and J_B must be made by analogy with other compounds.

The spectra of the disubstituted fluorobenzenes

studied in the present work are those due to ABCX systems. Systematic analysis of an ABC system is not usually possible, as solutions to cubic secular equations are necessary to obtain energy levels. Analysis of such systems has been accomplished using an iterative computor programme (SWALEN, REILLY 1962). In the present work the ^{19}F spectra approximated to the X part of a first order spectrum (AMPX) and was analysed as such. In some cases the effect of the substituents was to 'spread out' the ring proton resonance, so that a complete first order analysis was possible.

Discussion of the Spectra Obtained in the Present Work

The ^{19}F and ^{1}H nuclear magnetic resonance spectra discussed here are described in detail at the end of the chapter.

The spectra of the polychloropolyfluorobenzenes provided an unambiguous determination of their structures, where these were unknown. This was achieved using the relationships between ortho, meta and para coupling constants already described. In every case, except two, the chemical shift of an ^{19}F nucleus could be positively assigned, from a knowledge of the coupling constants in the multiplet. In the case of o-dichlorotetrafluorobenzene the coupling constants, together with a comparison of related molecules decided the assignment. The

chemical shifts in C_6HF_5 were assigned by comparison with those in C_6ClF_5.

^{19}F Chemical Shifts in Polyfluorobenzene Derivatives

The chemical shifts of the ^{19}F nuclei were found to vary in a characteristic way, according to the nature of the ortho, para and meta substituents. Table III,1 shows the effect of ortho and para F and Cl atoms on the chemical shift.

Table III,1

Effect of ortho and para F and Cl substituents on the chemical shift

Ortho substituent	F,F	F,F	F,Cl	F,Cl	Cl,Cl	Cl,Cl
Para substituent	F	Cl	F	Cl	F	Cl
Average chemical shift (ppm.)	162.1	155.7	138.2	133.0	116.4	112.5
No. of examples	5	3	4	3	2	1
Range of values (ppm.)	2.5	1.0	5.0	4.3	4.1	-

All chemical shifts are relative to CCl_3F, resonance occurring upfield from CCl_3F in every case.

It is apparent that for a given ring positions, the presence of a fluorine atom produces greater shielding of the ^{19}F nucleus than does a chlorine atom, and that the effect of an ortho substituent is far greater than that of a para substituent. Tables III,2, III,3 and III,4 show the effect on the ^{19}F chemical shift of replacing an

F atom by a Cl, in the ortho, para and meta ring positions respectively. The effect of replacing F and Cl by hydrogen are also shown. Columns 2, 3, 6 and 7 of the tables show diagrammatically the molecules from which the chemical shifts were obtained, the ^{19}F nucleus referred to being always at the bottom of the ring. A negative sign for the change in shift indicates a deshielding of the nucleus.

Table III, 2

The effect on the ^{19}F chemical shift of changing an ortho substituent

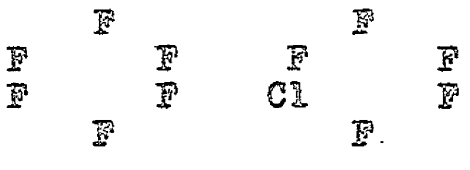
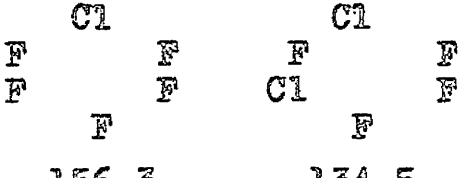
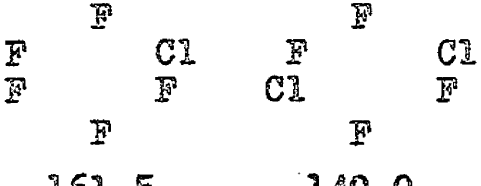
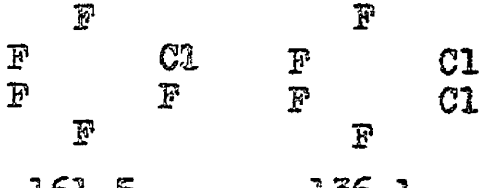
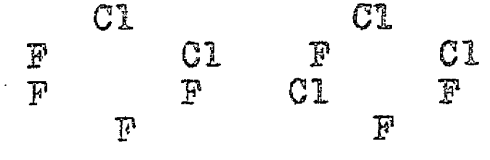
No.	Molecules involved in change and shifts (ppm.)	Change in shift (ppm.)	No.	Molecules involved in change and shifts (ppm.)	Change in shift (ppm.)
1.	 163.1 140.8	-22.3			
2.	 156.3 134.5	-21.8			
3.	 161.5 140.0	-21.5	4.	 161.5 136.1	-25.4

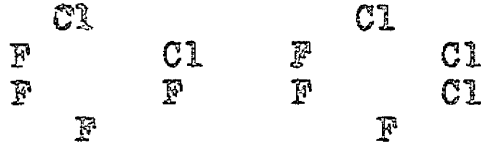
Table III, 2 contd.

5.



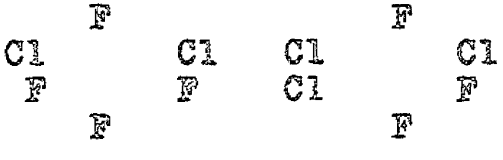
155.6	134.2	-21.4

6.



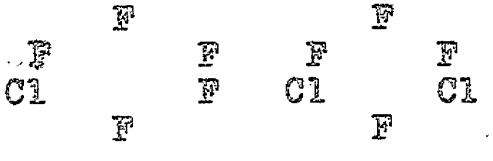
155.6	130.2	-25.4

7.



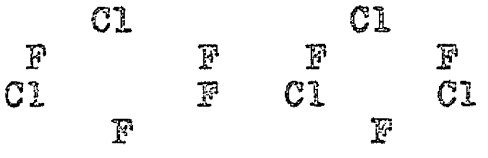
160.6	135.8	-24.8

8.



140.8	118.4	-22.4

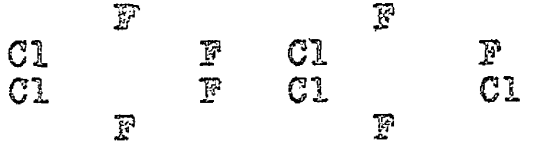
9.



134.5	112.5	-22.0

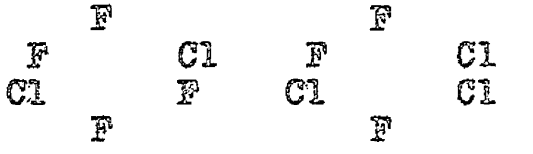
Table III, 2 contd.

10.



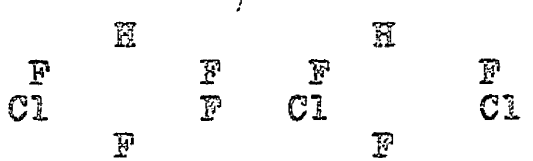
136.1 114.3 -21.8

11.



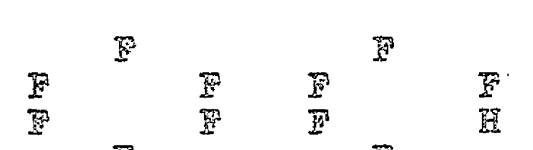
140.0 114.3 -25.7

12.



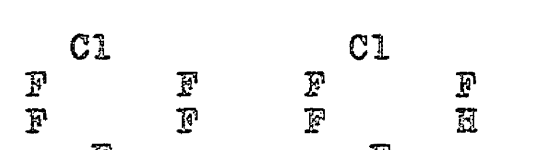
132.1 110.3 -21.8

13.



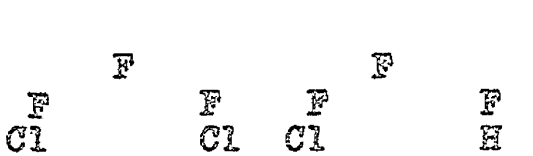
163.1 139.4 -23.7

14.



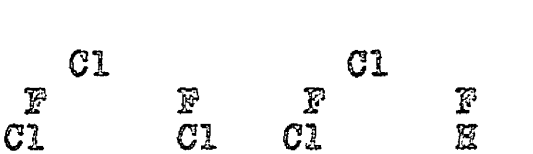
156.3 133.7 -22.6

15.



118.4 116.9 -1.5

16.



112.5 111.9 -0.6

Table III. 3

The effect on the ^{19}F chemical shift of changing a para substituent

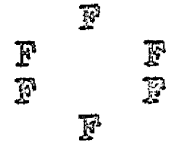
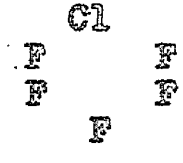
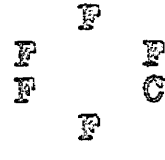
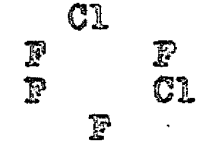
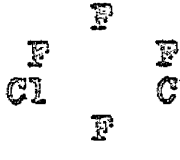
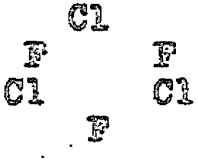
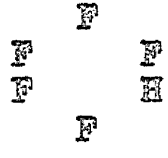
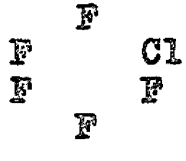
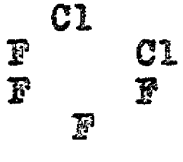
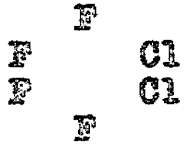
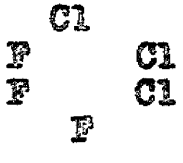
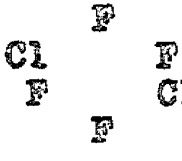
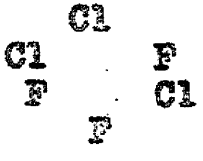
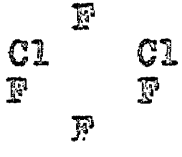
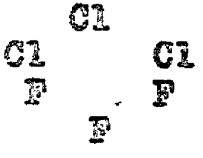
No.	Molecules involved in change and shifts (ppm.)		Change in shift (ppm.)
1.			
	163.1	156.3	-6.8
2.			
	140.8	134.5	-6.3
3.			
	118.4	112.5	-5.9
4.			
	139.4	133.7	-5.7
6.			
	161.5	155.6	-5.9
7.			
	136.1	130.2	-5.9
8.			
	140.0	134.2	-5.8
9.			
	160.6	155.3	-5.3

Table III. 3 contd.

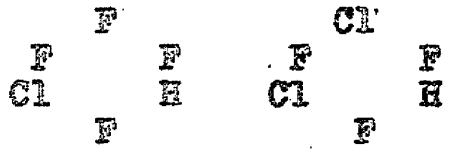
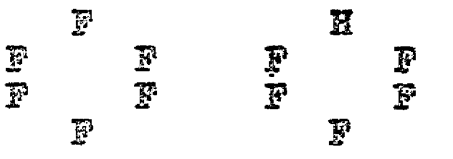
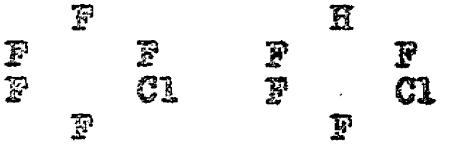
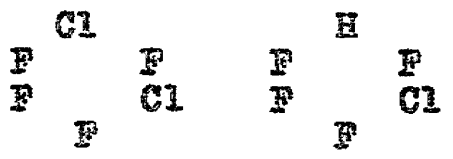
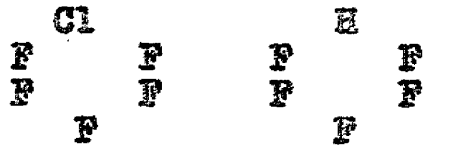
5.		116.9		111.9	-5.0		
10.		163.1		154.5	-8.6		
11.		140.8		132.1	-8.7		
12.		134.5		132.1	-2.4		
13.		156.3		154.5	-1.8		

Table III. 4

The effect on the ^{19}F chemical shift of changing a meta substituent

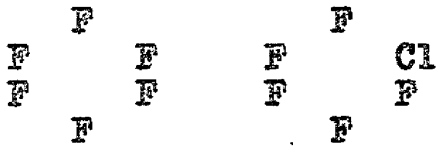
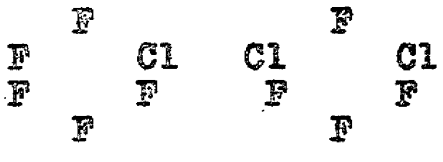
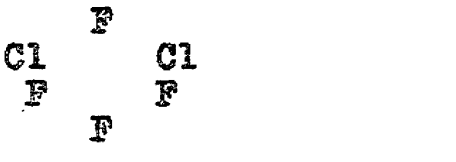
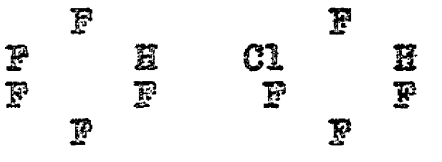
No.	Molecules involved in change and shifts (ppm.)		Change in shift (ppm.)	No.	Molecules involved in change and shifts (ppm.)		Change in shift (ppm.)
1.							
	163.1	161.5	-1.6				
2.							
	161.5	160.6	-0.9				
3.							
	163.0	162.3	-0.7				

Table III. 4 contd.

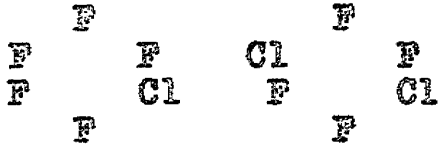
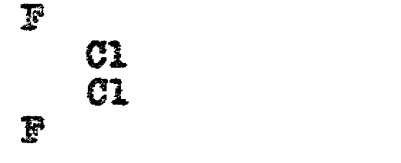
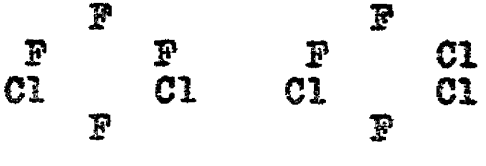
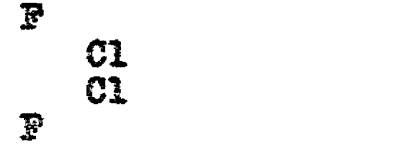
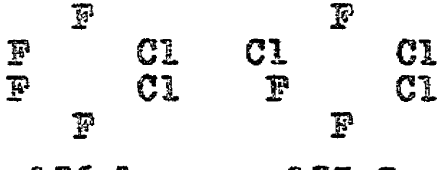
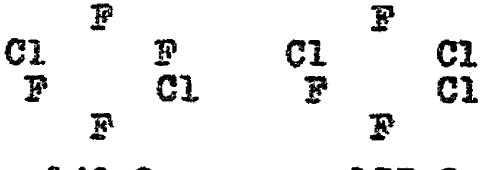
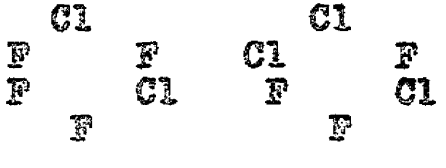
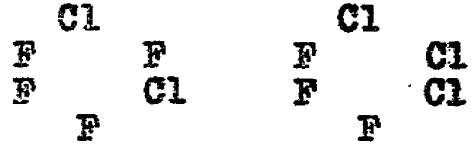
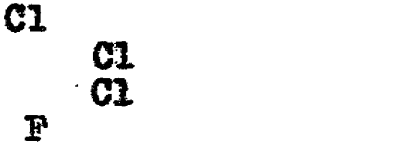
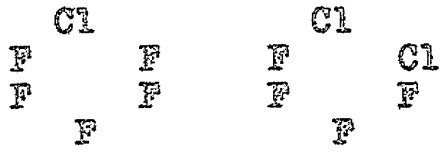
4.		140.8		140.0	-0.8
5.		140.8		136.1	-4.7
6.		118.4		114.3	-4.1
7.		136.1		135.8	-0.3
8.		140.0		135.8	-4.2
9.		134.5		134.2	-0.3
10.		134.5		130.2	-4.3

Table III, 4 contd.

11.

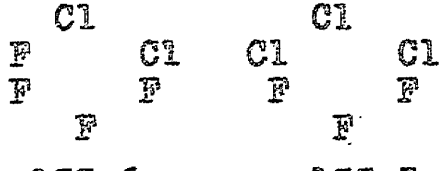


156.3

155.6

-0.7

12.

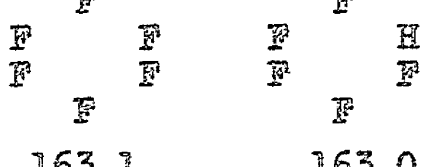


155.6

155.3

-0.3

13.

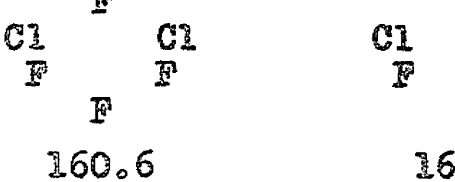


163.1

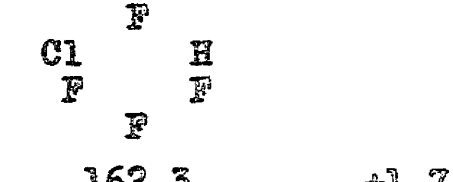
163.0

-0.1

14.



160.6



162.3

+1.7

The effect of the substitution, Cl for F, on the ^{19}F chemical shift decreases in the order, ortho > para > meta. In each case the substitution produces a deshielding of the ^{19}F nucleus. Large variations in the ^{19}F chemical shift of fluorobenzene derivatives due to ortho substituents have been reported in ortho substituted fluorobenzenes (GUTOWSKY, McCALL, McCARVEY, MEYER 1952) in polyfluorobenzenes (KARPLUS, DAS 1961) and in (pentafluorophenyl) organometallic compounds (BOURN, GILLIES, RANDALL 1963). The latter workers have suggested that the additional ortho shift, after allowance has been made for inductive and mesomeric effects, is due to the occupation of low lying unoccupied orbitals of the group ortho to the fluorine atom.

Using the treatment of KARPLUS and DAS to explain ^{19}F shielding in polyfluorobenzenes, the deshielding that occurs when a Cl atom is substituted for an F atom in the ring, can be explained qualitatively either by a decrease in the ionic character of the bonding F orbital or by an increase in the π-character of the bonding F orbital. KARPLUS and DAS have suggested that the large 'ortho effect' of an F atom on the chemical shift of an ^{19}F nucleus is due to electrostatic interaction between the two fluorine atoms. Such an interaction would be expected to be smaller between Cl and F atoms, resulting

in a deshielding of the ^{19}F nucleus when Cl is substituted for F.

The deshielding of the ^{19}F nucleus by an F->Cl substitution can also be explained (using PROSSER and GOODMAN'S treatment) on the basis of a decrease in the π-electron density of the conjugating F orbital and a decrease in the C—F π-electron bond order.

The difference in shielding between a para-fluoro, and a para-chloro substituted fluorobenzene, calculated using TAFT'S correlation equations, is smaller than the average value obtained in the present work, although the shielding effect is in the same direction. For meta substitution, an increase in shielding of the ^{19}F nucleus going from F to Cl is expected on the basis of TAFT'S treatment. In the present work the reverse is the case. It is apparent that in polysubstituted fluorobenzenes the effect of a substituent on the chemical shift is modified by the other substituents. It has been reported (GUTOWSKY, McCALL, McGARVEY, MEYER 1952) that shielding parameters (relative to PhF) calculated for meta and para polysubstituted fluorobenzenes, assuming the effects of the substituents to be additive, deviate from the experimental values. In the present work the experimental values of the shielding parameters have been found to be greater than those calculated.

The effect on the ^{19}F chemical shift of an F → Cl ortho substitution (the ortho effect) depends upon the nature of the meta substituents, and to a lesser extent on the para. (The terms ortho, meta and para refer to the F nucleus whose chemical shift is being studied). The 'ortho effect' falls into two classes, the average values being -21.9ppm. (range of 1.0ppm. over 8 values), and -25.3ppm. (range of 0.9ppm. over 4 values). In the former case the meta atom adjacent to the ortho position substituted is fluorine, in the latter case it is chlorine. The effect of the para atom is small, being comparable with errors in shift measurement due to solvent effects. It appears, however, that the 'ortho effect' is greater (by ≈ 0.5ppm.) when the para atom is fluorine.

The magnitude of the 'para effect' (defined in the same way as the ortho effect) depends upon the nature of the meta and ortho substituents. It is greatest when the meta atoms are fluorine and decreases with increasing meta Cl substitution. The magnitude also decreases with increasing number of Cl or H ortho substituents, this being shown in Nos. 1, 2, 3, 4 and 5 of Table III,3. It appears that both effects have approximately the same weight in affecting the magnitude.

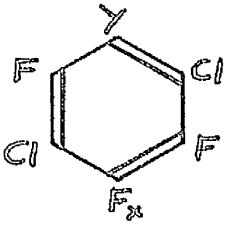
If the ortho and meta substituents are constant, para effects are additive i.e. para F→H = para F→Cl

+ para Cl⇒H. In Table III, 3 (11) = (2) + (12) and (10) = (1) + (13).

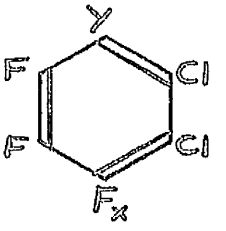
The magnitudes of the meta effects again fall into two groups, the average values being -0.7ppm. (range of 1.3ppm. over 8 values) and -4.3ppm. (range of 0.6ppm. over 4 values). In the former case the adjacent ortho atom is F and in the latter it is Cl. Cl⇒H meta substitution increases the shielding of the ^{19}F nucleus, in agreement with monosubstituted meta fluorobenzenes.

The two groups of 'ortho' and 'meta' effects arise from the fact that molecules of type (A) and (B) have values for the chemical shift of F_x that differ by about 3—4ppm., type (B) always appearing at lower field.

(A)



(B)



The nature of the para substituent does not affect this relationship greatly. Calculation of inter-nuclear distances suggests (COULSON, STOCKER 1959) that in benzene molecules, two ortho chlorine atoms result in the molecule being overcrowded, while two ortho fluorines do not. Ortho chlorine and fluorine atoms just produce overcrowding. It is possible to relieve this strain in an overcrowded molecule by opening out the XCCX' bond

region, while keeping the molecule planar. Experimental evidence is consistent with the fact that this occurs in 1,2,4,5 tetrachlorobenzene (GAFNER, HERBSTEIN 1958). In fully substituted molecules such strain could not be removed merely by widening the ClCCCl bond system and the difference in strain between (A) and (B) could account for the difference in shift.

Although the factors affecting the ^{19}F chemical shifts in these compounds are many, there is a clear empirical relationship between the chemical shift and the ortho and para substituents (Table III,1). This was used, together with a knowledge of the coupling constants, to determine the structures of five polychloropolyfluorophenols. The spectra and structures of these compounds are described at the end of the chapter.

^{19}F-^{19}F Coupling Constants

The values obtained here are not completely unbiased since many of them have been assigned from a knowledge of their approximate values. However, they make a self consistent body of evidence, the average values being: ortho 20.4 (11), meta 2.3 (11) and para 8.4cps. (7). The figures in parentheses denote the number of values on which the average is based. The spread of coupling constants is as follows: ortho 2.0, para 3.4 and meta 4.6cps. In two cases it was possible

to determine the relative signs of two pairs of coupling constants; J^{o}_{FF} and J^{p}_{FF} are of opposite sign in chloropentafluorobenzene and J^{o}_{FF} and J^{m}_{FF} are of opposite sign in 1,2-dichlorotetrafluorobenzene. This is in agreement with the work of EVANS (1962a) who found, by double resonance experiments, that J^{o}_{FF} has opposite sign to J^{m}_{FF} and J^{p}_{FF} in 1,2-dichloro-3,4,6-trifluorobenzene and in 1-chloro-2-nitro-3,4,6 trifluorobenzene. There seems to be no simple relationship between the magnitude of a coupling constant and the other ring substituents, although the variation in value of J^{m}_{FF} is quite large (i.e. 0.7 - 5.3cps.).

^{19}F Chemical Shifts in Disubstituted Fluorobenzenes

In view of the complicated nature of ^{19}F shielding in polysubstituted fluorobenzenes, some methyl and carboxylic ester derivatives of fluorobenzene were studied. The effect on the ^{19}F chemical shift of mono-substitution in the ortho, meta and para positions was compared with the effect of di- and tri- substitution in various ring positions. Tables III,5, III,6 and III,7 show the substituent effect on the chemical shift (relative to PhF). The chemical shift of PhF was taken as 113.1ppm. (FILLIPOVITCH, TIERS 1959) and a positive value of the experimental shielding parameter ($\triangle_E$) indicates that resonance occurred upfield from PhF. Solvent effects

were minimised by running all spectra under equivalent conditions as far as possible. The additive shielding parameter ($\triangle_A$ ppm.) is the sum of the separate experimental shielding parameters, obtained from the monosubstituted fluorobenzenes. The difference ($\triangle_E - \triangle_A$)ppm. is thus a measure of the interaction between the substituents.

The ortho and para effect of -Me and of $-CO_2Me$ substituents are approximately equal. The products obtained from aromatic substitution reactions in which inductive and mesomeric directing effects are operative, suggest that the chemical shifts are due to inductive and mesomeric contributions only. In both cases, however, the ortho shielding parameter is less than the para when the reverse should be the case. A possible explanation for this is that the electronic effects are inhibited by the substituent being twisted out of the plane of the ring, due to steric repulsion. That this is so with ortho $-CO_2Me$ substituents is suggested because the difference $\triangle_E - \triangle_A$ = +1.7 for dimethyl-2-fluoro-isophthalate. There is evidence (TAFT 1956) that the presence of adjacent methyl groups (2,6 disubstituted) inhibits the resonance of dimethylamino, carboxyl and nitro groups with the benzene ring. The steric repulsion is such that the reactive group ($\cdot NMe_2$, $\cdot CO_2H$ etc.) cannot be

Table III, 5

Effect on the ^{19}F Chemical Shift of Methyl Substituents

Position of substituent(s)	Expt. shielding parameters Δ_E (ppm.)	Additive shielding parameter Δ_A (ppm.)	Difference $(\Delta_E - \Delta_A)$ ppm.
ortho	+4.6	-	-
meta	+1.2	-	-
para	+5.4	-	-
ortho + ortho	+9.1	+9.2	-0.1
ortho + meta	+5.7	+5.8	-0.1
ortho + meta (adjacent)	+5.0	+5.8	-0.8
ortho + para	+10.0	+10.0	-
meta + para	+5.4	+6.6	-1.2

Table III, 6

Effect on the ^{19}F Chemical Shift of Carboxylic Methyl Ester Substituents

Position of substituents	Expt. shielding parameter $\triangle_E$ (ppm.)	Additive shielding parameter $\triangle_A$ (ppm.)	Difference ($\triangle_E - \triangle_A$) ppm.
ortho	-4.1	-	-
meta	-0.3	-	-
para	-6.4	-	-
ortho + ortho	-6.5	-8.2	+1.7
ortho + meta	-4.7	-4.4	-0.3
ortho + meta (adjacent)	+2.7	-4.4	+7.1
ortho + meta (anhydride)	-3.9	-4.4	+0.5
ortho + para	-10.4	-10.5	+0.1
meta + para	-5.2	-6.7	+1.5
meta + para (anhydride)	-14.8	-6.7	-8.1

Table III. 7

Effect on the ^{19}F Chemical Shift of Nitro and Methyl Substituents

Position and nature of substituent	Expt. shielding parameter $\triangle_E$ (ppm.)	Additive shielding parameter $\triangle_A$ (ppm.)	Difference ($\triangle_E - \triangle_A$) ppm.
ortho nitro[a]	+5.6	-	-
meta nitro	-3.4	-	-
para nitro	-9.9	-	-
(ortho + para) nitro	-5.9	-4.3	-1.6
(ortho + meta) methyl + para nitro	-2.5	-4.1	+1.6
(ortho + meta) methyl adjacent + para nitro	-3.5	-4.1	+0.6

(a) GUTOWSKY, McCALL, McGARVEY, MEYER (1952).

coplanar with the ring.

When the substituents in a disubstituted fluoro-benzene are not adjacent to each other, their effect on the ^{19}F chemical shift is equal to the sum of the separate shielding parameters. Two adjacent substituents affect each other, the result being that the electron donating or attracting power of the substituents is inhibited. The fluorophthalic anhydrides are anomolous in this respect, particularly 4-fluorophthalic anhydride. The ^{1}H and ^{19}F resonances of both anhydrides are shifted downfield compared to those of the corresponding dimethyl esters. The proton and ^{19}F downfield shifts are 0.20 and 6.6ppm. for 3-fluoro-phthalic anhydride, and 0.40 and 9.6ppm. for 4-fluoro-phthalic anhydride. The addition of the anhydride ring deshields both the protons and the ^{19}F nucleus.

Effect of the Fluorine Atom on Proton Chemical Shifts

The presence of a fluorine atom in an aromatic molecule increases the shielding of the protons ortho to it, relative to those of the hydrogen analogue. This is particularly noticeable in poly-fluoro-compounds containing one proton. The chemical shifts of methyl protons in fluoro toluenes and xylenes are affected by a fluorine atom, as they are more shielded than those in the corresponding toluene or xylene. The shielding

decreases in the order ortho > meta > para. The methyl proton peaks in the $-CO_2Me$ compounds were assigned on this basis but here the effect is very small.

Conclusion

The effect of a substituent on the ^{19}F chemical shift of a polysubstituted fluorobenzene depends upon its ring position, size and electronic properties. The substituent's effect is modified by the atoms adjacent to it, and for this reason the shifts do not fit the empirical Hammett function treatment that applies to meta and para mono-substituted fluorobenzenes. The different effects that F and Cl substituents have on the ^{19}F chemical shift arise from the fact that Cl is larger than F, that the inductive effect of F is greater than that of Cl, and that the mesomeric effect of F is far greater than that of Cl. The mesomeric effect of the F atom seems to be responsible for the increase in shielding experienced by the ring protons and methyl protons in fluoroxylenes. The magnitudes of ^{1}H-^{19}F and ^{19}F-^{19}F coupling constants are characteristic of the relative positions of the nuclei. This makes them useful in the determination of structures from N.M.R. spectra.

EXPERIMENTAL

The polychloropolyfluorobenzenes and phenols (except C_6F_6 and C_6HF_5) were a gift from Imperial Chemical Industries Ltd. (Alkali Division). The fluoro-toluenes, xylenes and carboxylic acids (except p-F. $C_6H_4CO_2H$) were a gift from Dr. G. Valkanas (Technisch-chemisches Laboratorium, Zurich). The remaining compounds were commercial samples.

^{19}F nuclear magnetic resonance spectra were recorded at 37.65 Mc/s on a Perkin Elmer spectrometer. Proton spectra were recorded at 40.00 Mc/s on the same instrument. Both resonances were observed at a temperature of 33.5°C. The resolution of the instrument was better than $1:10^8$ but the natural line width of the samples prevented this being attained in the fluorine spectra. The liquid samples were run as 30% solutions (by volume) in carbon tetrachloride. In the case of the solid phenol, the nitro-fluoro-xylenes and 2,4dinitrofluorobenzene, 100mg. of the compound were dissolved in 2ml. of carbon tetra-chloride to make up the solution used.

The carboxylic acids (200mg. of each compound) were esterified with diazomethane (Collective Organic Syntheses 2 166) and the methyl ester produced diluted with carbon tetrachloride. The two fluoro-phthalic anhydrides

were converted to the acid by refluxing 200mg. of the anhydride for several hours, with a mixture of methanol and sulphuric acid (1:1 by volume). Methylation was completed by treatment with diazomethane.

Except for the chlorofluorophenols, ^{19}F spectra were referenced internally to CCl_3F (δ being used to denote the shift in ppm.) using either a side band technique or the decade shift and calibrated chart of the instrument. It was found that both methods were equally accurate. The phenols were referenced externally to benzotrifluoride and 63.5ppm. was added, to reference the peaks relative to CCl_3F. Resonance occurred up-field from CCl_3F in every case. Proton spectra were referenced internally to tetramethylsilane (the τ scale being used to denote the shift). The separations in the multiplets were measured using dividers and a rule equipped with a vernier scale. Coupling constants are accurate to $\pm$0.2cps, ^{19}F chemical shifts to $\pm$0.15ppm. and ^{1}H chemical shifts to $\pm$0.02ppm. All values of the spectral parameters obtained in this work are averaged values from several determinations.

Where samples were mixtures of different isomers, the nuclear magnetic resonance spectra of different distillation or chromatographic fractions served to identify peaks from a particular molecule.

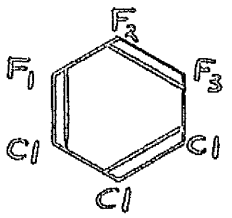
The notation used to describe the coupling constants (J cps.) is as follows: the relationship between the nuclei (ortho, meta or para) is denoted by the superscript, whilst the nature of the nuclei (H, F or methyl protons) is denoted in the subscript. Where more than one ^{1}H or ^{19}F nucleus is present, the ring number only of the nucleus serves to identify it. Whenever the relative signs of coupling constants could be obtained they are indicated. In the other cases, the signs were not obtained.

NUCLEAR MAGNETIC RESONANCE SPECTRA, COUPLING CONSTANTS AND CHEMICAL SHIFTS

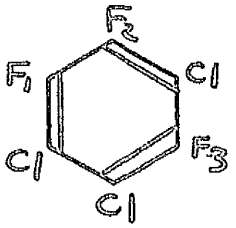
(A) Polyfluorobenzene Derivatives

Trichlorotrifluorobenzenes

Pure samples of the three isomers were not available but two mixtures containing the isomers (I), (II) and (III) in the proportions (a) 13:54:33 and (b) 30:10:60, were examined. Using the integral curve, the spectra of the mixtures were assigned without difficulty.



(I)



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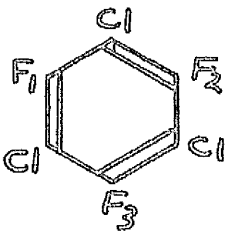


(III)

1,2,3-Trichlorotrifluorobenzene(I) showed a doublet at 130.2ppm. due to F_1 and F_3 and a triplet at 155.3ppm. due to F_2. The coupling constant J^{o}_{12} = 20.9cps.

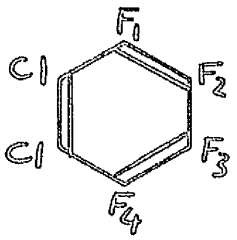
1,2,4-Trichlorotrifluorobenzene(II) showed a twelve line spectrum characteristic of an AMX system, the resonance due to each F atom being a pair of doublets. Values for the spectral parameters obtained are as follows: chemical shifts F_1=135.8, F_2=134.2, F_3=114.3ppm. Coupling constants J^{o}_{12}=20.9, J^{p}_{13}=9.0, J^{m}_{23}=0.7 cps.

1,3,5-Trichlorotrifluorobenzene(III) showed a single line at 112.5ppm. It was not possible to identify the ^{13}C satallite peaks due to the presence of the spectra of

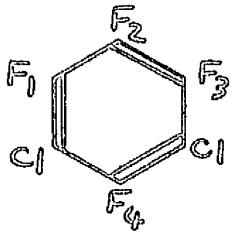
other isomers. Hence no value of J^{p}_{13} was obtained.

Dichlorotetrafluorobenzenes

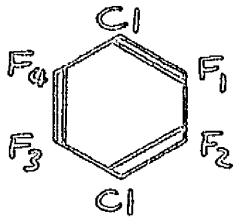
Except for meta-dichlorotetrafluorobenzene, pure compounds were not available but four mixtures were examined. Two contained the three isomers (IV), (V) and (VI) in the proportions (a) 22:59:19 and (b) 16:82:2. The other two contained isomers (IV) and (V) in the proportions (c) 15:85 and (d) 5:95 together with traces of isomer (VI).



(IV)



(V)



(VI)

p-Dichlorotetrafluorobenzene(VI) gave rise to a single peak at 140.0ppm.

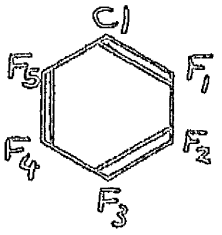
m-Dichlorotetrafluorobenzene (V) had a spectrum consisting of two overlapping 1:2:1 triplets at 160.6ppm., relative intensity 1, due to F_2, a pair of doublets relative intensity 2, at 134.5ppm., due to F_1 and F_3, and a pair of 1:2:1 triplets, relative intensity 1, due to F_4, at 118.4ppm. The coupling constants obtained were $J^{o}_{12}(=J^{o}_{23})=20.1$, $J^{p}_{24}=7.9$ and $J^{m}_{14}(=J^{m}_{34})=2.3$cps.

o-Dichlorotetrafluorobenzene(IV) gave rise to a spectrum characteristic of an A_2X_2 system where two nuclei (in

this case F_2 and F_3) are more strongly coupled than the other two (F_1F_4) (POPLE, SCHNEIDER, BERNSTEIN 1959). The two identical multiplets (see Fig. 3,1) were each symmetrical about their mid-points and each showed the expected ten lines. The low field multiplet at 136.1ppm. was assigned to F_1 and F_4 and the high field multiplet at 155.6ppm. to F_2 and F_3, by analogy with other compounds containing ^{19}F nuclei in similar environments. Coupling constants obtained were as follows: $J^o_{12}(=J^o_{34})=\pm 20.5$, $J^o_{23}=19.1$, $J^m_{13}(=J^m_{24})=\pm 2.5$ and $J^p_{14}=7.4$cps. The theoretical spectrum calculated using these values agreed well with the experimental spectrum.

Chloropentafluorobenzene(VII) The spectrum of pure (99%+) C_6ClF_5 was run as a neat liquid and as a 30% solution in carbon tetrachloride. The results were substantially the same in both cases, the only difference being in the values of the chemical shifts. Those reported are from the solution spectrum but the analysis of the multiplets was carried out from the spectrum of the undiluted material as this was somewhat clearer. The spectrum consisted of a 1:2:1 triplet (relative intensity 1) at 156.3ppm. due to F_3 and two complex multiplets (each of relative intensity 2) at 140.8 and 161.5ppm., which were assigned to F_1F_5 and F_2F_4 respectively. The observed and calculated spectra are shown in Fig. 3,2.

(VII)



Under conditions of very rapid scanning the multiplet at 161.5ppm. appeared to be a triplet but a slow scan indicated that it was one half of an A_2X_2 spectrum which had been further split by first order coupling with another nucleus (F_3). To analyse the A_2X_2 system this multiplet was examined, since from the triplet, the magnitude of the coupling between F_2, F_4 and F_3 was readily determined. The value obtained was $J^o_{23}(=J^o_{43})=19.6$cps. This was used to separate the two overlapping parts of the high-field multiplet and so complete the analysis. The following coupling constants were obtained: $J^o_{12}(=J^o_{45})=\pm 20.7$ and $J^p_{14}(=J^p_{25})=\mp 6.4$cps. It was not possible to distinguish between the two meta coupling constants J^m_{15} and J^m_{24} or to obtain their relative signs. The values obtained were 5.3 and 2.0cps.

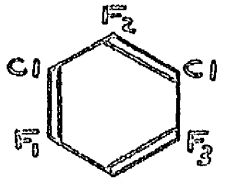
Coupling between F_3 and F_1 (and F_5) was barely detectable in the spectrum of the pure liquid. It was responsible however for the diffuseness of the multiplet at 140.8ppm. (Fig.3,2). In the spectrum of the CCl_4 solution this coupling was apparent from the further splitting of each peak of the triplet at 156.3ppm. From

this splitting it was concluded that $J^{m}_{13}(=J^{m}_{35})$ = 1cps. An analysis of the low field multiplet assuming that J^{m}_{13} = 1cps. gave values of J^{o}_{12}, J^{p}_{14}, J^{m}_{15} and J^{m}_{24} that agreed to 0.1cps. with those derived from the high field multiplet.

The spectrum calculated using these parameters agreed well with the experimental spectrum.

Hexafluorobenzene showed a single line at 163.1ppm. No ^{13}C satellite peaks were observed.

1,3-Dichloro-2,4,6-trifluorobenzene (VIII) was known to be a pure sample of molecular formula $C_6HCl_2F_3$ but its orientation was unknown. This was unambiguously established by examination of the ^{1}H and ^{19}F spectra.

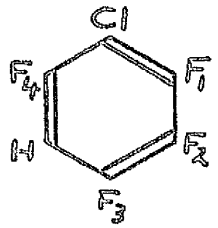


(VIII)

The proton spectrum was basically a 1:2:1 triplet at 3.06τ, due to the proton coupling with two equivalent ortho fluorines J^{o}_{H1}=8.6cps. Each peak of the triplet was further split due to coupling with a para fluorine, J^{p}_{H2}=2.3cps. The ^{19}F spectrum consisted of a double doublet (intensity 2) at 111.9ppm. and a group of four peaks (intensity 1) at 110.3ppm. These were assigned to F_1 and F_3, and to F_2 respectively. The coupling constants obtained from the double doublet were

J^{o}_{H1}=8.6 and $J^{m}_{12}(=J^{m}_{23})$=1.9cps. The four peaks at 110.3ppm. were, in reality, two overlapping triplets; the closeness of the coupling constants, J^{p}_{H2}=2.3 and $J^{m}_{12}(=J^{m}_{23})$=1.9cps., prevented all the peaks being observed.

1-Chloro-2,3,4,6-tetrafluorobenzene(IX). This compound was available in a substantially pure state as a liquid of known molecular formula but of unknown orientation. The structure was elucidated from studies of its ^{1}H and ^{19}F spectra.



(IX)

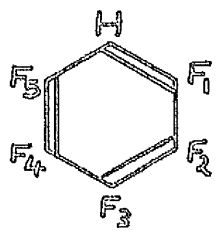
The proton resonance spectrum contained a set of fourteen peaks symmetrical about its mid-point at 3.06τ. Sixteen peaks would be expected for a proton coupled to four non-equivalent ^{19}F nuclei in a first order spectrum. Two of the peaks were twice as intense as the rest, so it was presumed that in two cases two peaks were coincident. The ^{19}F spectrum consisted of four multiplets centred at 116.9, 132.1, 133.7 and 162.3ppm. Each of the multiplets should consist of sixteen peaks from coupling with four non-equivalent nuclei but the similarity of the

coupling constants prevented all of the peaks from being observed. In particular the resonance at 116.9ppm. consisted of a 1:2:1 triplet, each peak further split into a triplet, the splittings (9.0 and 1.1cps.) being the average of $J^{o}_{HF_4}$, J^{p}_{24} and J^{m}_{14}, J^{m}_{34} respectively.

The first order analysis of the spectra gave the chemical shifts and coupling constants of Table III,8. Spectra calculated using the average values of the coupling constants agreed well with the experimental spectra. Both are shown in Fig.3,3.

The alternative structures for this compound involving ortho or para orientation of the hydrogen and chlorine atoms can be ruled out; the former would have a ^{19}F spectrum involving three ortho ^{19}F-^{19}F coupling constants, whilst the latter would have an A_2M_2X spectrum, which could not be interpreted using first order methods.

Pentafluorobenzene(X) The ^{1}H spectrum of this compound consisted of a set of eighteen peaks symmetrical about its mid point at 3.06τ. This was analysed by first order methods as the X part of an A_2M_2PX system.



(X)

Table III. 8

Chemical shifts and coupling constants in 1-chloro-2,3,4,6-tetrafluorobenzene (IX).

Resonance	H	F_1	F_2	F_3	F_4
Chemical Shift	3.06 (τ)	132.1 (δ)	162.3 (δ)	133.7 (δ)	116.9 (δ)
Coupling constants (J) in cps.	10.0 HF_3	19.9 F_1F_2	20.7 F_3F_2	20.7 F_3F_2	9.0 F_4H, F_4F_2
	8.8 HF_4	4.9 F_1F_3	19.9 F_2F_1	9.8 F_3H	
	6.4 HF_2	2.6 F_1H	9.8 F_2F_4	4.9 F_3F_1	1.1 F_4F_1, F_4F_3
	2.8 HF_1	1.5 F_1F_4	6.4 F_2F	0.9 F_3F_4	

Averaged values of J's

$J^{p}_{H1} = 2.7$ $J^{m}_{H2} = 6.4$ $J^{o}_{H3} = 9.9$ $J^{o}_{H4} = 8.9$ $J^{o}_{12} = 19.9$

$J^{m}_{13} = 4.9$ $J^{m}_{14} = 1.3$ $J^{o}_{23} = 20.7$ $J^{p}_{24} = 9.8$ $J^{m}_{34} = 1.0$ cps.

Coupling constants evaluated were J^{o}_{HF}=10.2, J^{m}_{HF}=6.8 and J^{p}_{HF}=2.6cps. The ^{19}F spectrum was complex and was not analysed. However, the three complex multiplets (intensity ratio 2:1:2) were all approximately symmetrical about their mid points and these were taken as the chemical shifts of the nuclei. The multiplets were assigned using the intensity ratio and by analogy with C_6ClF_5. Chemical shifts obtained were F_1F_5 at 139.4, F_2F_4 at 163.0 and F_3 at 154.5ppm.

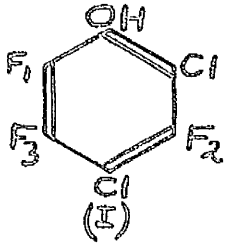
Where the present work overlaps with previous measurements the agreement is generally good. GUTOWSKY, HOLM, SAIKA and WILLIAMS (1957) have measured the coupling constants in 1,3-dichloro-2,4,6-trifluorobenzene and the results obtained here agree well with their values. Chemical shifts reported for several polychloropolyfluorobenzenes (BOURN, GILLIES, RANDALL 1963; CHAMBERS, HEYES, MUSGRAVE 1963) agree fairly well with present work. The value of 98ppm. reported for the chemical shift of 1,3,5-trichlorotrifluorobenzene (MULLER, CARR 1963) does not agree with the present work.

(B) Polyfluorophenols

All these samples were compounds (or mixtures of isomers) of which the molecular formula was known but whose structure(s) were not. The nuclear magnetic resonance spectra did not afford an unambiguous assignment

solely on the basis of the magnitude of the coupling constants. By using the empirical relationships between substituents and chemical shift developed in this work and assuming that the effect of an hydroxyl group is similar to a fluorine atom, a set of structures were deduced for which the chemical shifts were internally consistent. The shifts presented for these compounds are not completely unbiased but their consistency indicates that the structures deduced are correct.

2,4,-Dichloro-3,5,6-trifluorophenol(I) This was shown to be a pure compound of m.p. 45-6°C. Its ^{19}F spectrum consisted of three sets of four peaks characteristic of a first order AMX spectrum. The coupling constants obtained showed the presence of a 1,2,4 orientation of the fluorine atoms. If the shielding effects of F and OH are similar, the structure must be (I).



(I)

Chemical shifts and coupling constants obtained were F_1 at 160.5, F_2 at 118.4 and F_3 at 135.8ppm; J^{o}_{13}=21.1, J^{p}_{12}=8.5 and J^{m}_{23}=1.9cps.

Trichlorodifluorophenols

A liquid mixture of these compounds was studied and

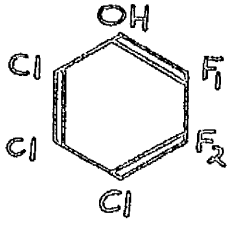
the presence of four components was shown, using the integral curve to pick out peaks due to different nuclei in the same isomer.

2,3,4-Trichloro-5,6-difluorophenol(II) showed two doublets at 131.5 (due to F_2) and 154.8ppm. (due to F_1). The coupling constant J^{o}_{12}=21.1cps.

2,4,5-Trichloro-3,6-difluorophenol(III) showed two doublets at 114.5 (due to F_1) and 135.9ppm. (due to F_2). The coupling constant J^{p}_{12}=9.8cps.

3,4,5-Trichloro-2,6-difluorophenol(IV) showed a single peak at 131.0ppm.

2,4,6-Trichloro-3,5-difluorophenol(V) showed a single peak at 112.6ppm.



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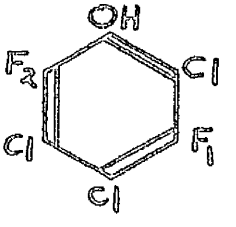

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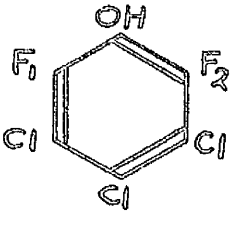
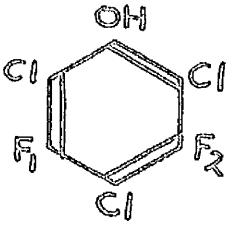


(IV)



(V)

(C) Methyl Derivatives of Fluorobenzene

In general the spectra of these compounds were not so well defined as those of the polyfluorobenzenes, possibly due to the fact that many of the coupling constants in a molecule are of similar magnitude. In the cases where a full analysis could be carried out, the spectra approximated to first order systems, so the errors in the parameters obtained are not large. The mid point of the ^{19}F resonance was taken to be identical with the chemical shift. Small errors ($\leqslant$ 8cps.) could occur in the chemical shifts when the spectra were not first order.

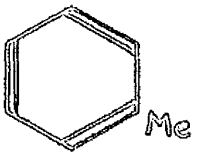
o-Fluoro-toluene(I) The ring proton resonance consisted of two strong peaks at 3.01 and 3.13 τ with some fine structure, due to the ABCD part of an ABCDX system. The methyl proton resonance consisted of a doublet at 7.83 τ. The separation gave J^{o}_{FMe}=2.8cps. The ^{19}F resonance was a complex set of peaks at 117.7ppm. due to the X part of an ABCDX system further split due to proton-fluorine coupling.

m-Fluorotoluene(II) had a complex signal due to the ring protons, the ABCD part of an ABCDX system. The position of the strongest peak was at 3.14τ. The methyl group resonance consisted of a single peak (broadened) at 7.75τ. The ^{19}F resonance, the X part of an ABCDX

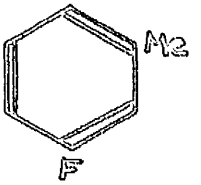
system, consisted of six peaks, each being further split, and the multiplet was approximately symmetrical about its mid-point at 114.3ppm.

<u>p-Fluorotoluene(III)</u> had a ring proton signal consisting of a single peak at 3.04 τ and a doublet at 3.22 τ. The methyl resonance was a single peak (broadened) at 7.78 τ. The ^{19}F resonance was a 1:4:6:4:1 quintette, each peak being further split into four, giving J^{p}_{FMe}=1.0cps. The simplest explanation of the ^{19}F spectrum is that all the hydrogen atoms are magnetically equivalent giving $J^{o}_{HF}=J^{m}_{HF}$=6.9cps. This explanation has previously been advanced to explain the spectrum observed for liquid p-fluorotoluene (SCHAEFER 1959). However, when the spectrum is run in different solvents, its appearance changes and the protons become non-equivalent (SCHAEFER, SCHNEIDER 1959). The coupling constants obtained in this case are J^{o}_{HF}=8.7 and J^{m}_{HF}=5.8cps. It has been suggested (ABRAHAM, BERNSTEIN 1961) that deceptively simple spectra, such as that obtained with p-fluorotoluene, will arise quite logically in an ABX system where the coupling constants $J_{AB'}$, $J_{AX'}$, $J_{BX'}$ are approximately equal. The line width at half height of the peaks then becomes an important factor in determining the shape of the observed spectrum. The separation of the quintette peaks should be the average

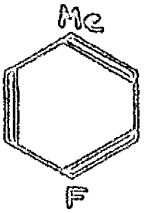
of J_{AX} and J_{BX} and that obtained in the present work agrees reasonably well with this. The spectra of fluorotoluenes have been reported previously (RICHARDS, SCHAEFER 1958) and the parameters reported agree fairly well with those obtained here.



(I)

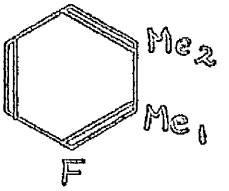


(II)



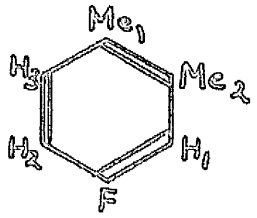
(III)

3-Fluoro-1,2-xylene(IV) had a ring proton resonance consisting of a strong doublet, centred at 3.23τ, together with some fine structure. This was due to the ABC part of an ABCX system. The methyl proton resonance was a single peak at 7.89τ and a doublet (partially obscured by the single peak) at 7.95τ. The separation of the doublet peaks was 2.8cps., so the resonance at 7.95τ was assigned to the ortho Me_1 group and that at 7.89τ to the meta Me_2 group by analogy with the Me-F coupling constants of other methyl derivatives.



(IV)

4-Fluoro-1,2-xylene(V) The ring proton resonance of this compound consisted of two strong peaks at 3.16 τ and 3.38 τ together with some fine structure. The methyl proton resonance was a single peak (broadened) at 7.82 τ.

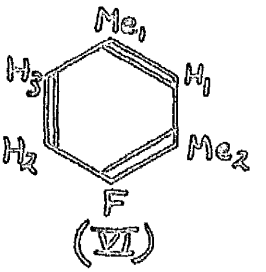


(V)

The ^{19}F spectrum consisted of a 1:3:3:1 quartette at 118.5ppm. each peak of which was further split into four peaks. This smaller splitting was assigned to F-Me_2 coupling, giving $J^{m}_{FMe_2}$=0.9cps. The quartette splitting (8.3cps.) could either be explained in terms of magnetic equivalence of the protons, giving $J^{o}_{F1}=J^{o}_{F2}=J^{m}_{F3}$=8.3cps., or, more convincingly, using the method due to ABRAHAM and BERNSTEIN (1961). In this case $1/3(J^{o}_{F1}+J^{o}_{F2}+J^{m}_{F3})$=8.3cps., the splitting representing the average value of the three fluorine-ring proton coupling constants.

4-Fluoro-1,3-xylene(VI) This had a ring proton resonance consisting of two broad peaks at 3.16 τ and 3.33 τ. The methyl proton resonance consisted of a single peak at 7.81 τ and a doublet, part of which was obscured by the single peak, at 7.87 τ; the doublet separation was $\sim$1.1cps. By analogy with the other compounds, the peak at 7.81 was assigned to Me_1 and the doublet to Me_2 giving

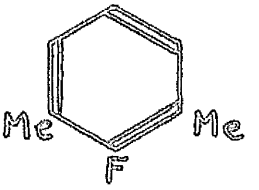
$J^{o}_{FMe_2} \sim 1.1$cps.



(VI)

The ^{19}F resonance showed a broad 1:3:3:1 quartette of peaks at 123.1ppm., the separation being 7.3cps. The peaks showed a further splitting of 1.1cps. confirming that $J^{o}_{FMe_2}$=1.1cps. By analogy with compounds (III) and (V) the splitting represents an average value of the three ^{19}F coupling constants i.e. $1/3(J^{o}_{F2} + J^{m}_{F1} + J^{m}_{F3})$=7.3cps

2-Fluoro-1,3-xylene(VII) had a ring proton resonance consisting of two peaks at 3.15 and 3.24τ. The methyl proton resonance was a doublet at 7.80τ giving J^{o}_{FMe}=2.4cps.

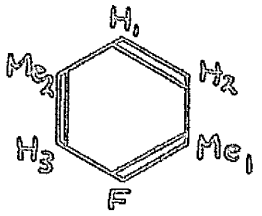


(VII)

The ^{19}F spectrum consisted of a complex set of peaks approximately symmetrical about its mid-point at 122.2ppm. This was not analysed.

2-Fluoro-1,4-xylene(VIII) The ring proton resonance consisted of four broad peaks of different intensity, due to the ABC part of an ABCX system. The mid-point of the

multiplet was at 3.18τ; and the position of the most intense peak was 3.27τ. The methyl proton resonance was a single peak at 7.81τ and a doublet, partially obscured by the single peak, at 7.85τ. The separation of the doublet peaks was approximately 2cps. By analogy with the other compounds, the chemical shifts were assigned as follows: Me_1 at 7.85, Me_2 at 7.81τ: $J^{o}_{FMe_1} \sim$ 2cps.

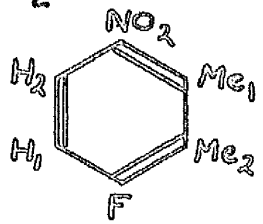


(VIII)

The ^{19}F resonance consisted of three groups of peaks, approximately symmetrical about the mid-point at 118.8ppm. The spectrum was analysed by approximation to the X part of a first order AMX system. This accounted for the larger splittings but not for the smaller. The coupling constants obtained were J^{o}_{F3}=10.2, J^{m}_{F2}=7.2cps.

3-Fluoro-6-nitro-1,2-xylene(IX)had a spectrum that was a good approximation to a first order AMX system, the fluorine spectrum being complicated by further coupling with the ortho methyl group. The ring proton resonance consisted of two doublets at 2.32τ (due to H_2) and a 1:2:1 triplet at 3.02τ (due to H_1). The doublet separations were 5.2 and 9.0cps. and the triplet separation

9.0cps. The methyl proton resonance consisted of a single peak at 7.58 τ (due to Me_1) and a doublet at 7.73 τ (due to Me_2) giving $J^{o}_{FMe_2}$=2.5cps.



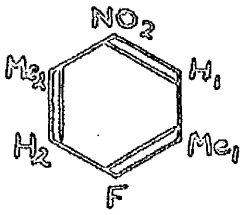
(IX)

The ^{19}F spectrum consisted of nine lines, symmetrical about the central line, at 109.6ppm. The intensities of the lines decreased from the centre, the two outermost lines being very weak. The multiplet was analysed as a set of four quartettes, the expected 16 lines not being observed due to overlapping. The coupling constants extracted were 8.5, 5.3 and 2.4cps. The good agreement obtained between the ^{1}H and ^{19}F spectra justifies this procedure.

The coupling constants obtained were:
J^{o}_{F1}=8.7(5), J^{m}_{F2}=5.3, J^{o}_{12}=9.0, $J^{o}_{FMe_2}$=2.5cps.

2-Fluoro-5-nitro-1,4-xylene(X) The ring proton resonance consisted of a pair of doublets at 2.11 and 3.03τ. The peak separations were 7.2 and 9.6cps. respectively, therefore the coupling between the para hydrogens must be $\sim$0cps. The resonance could thus be assigned as follows: H_1 at 2.11 τ and H_2 at 3.03 τ. The methyl proton resonance consisted of a single peak at 7.44 τ (due to Me_2)

and a partially resolved doublet at 7.68 τ (due to Me_1). The doublet separation was approximately 1.3cps.



(X)

The ^{19}F spectrum consisted of seven peaks symmetrical about the centre peak at 110.6ppm. Some unresolved peaks were also observed. The first order spectrum of a ^{19}F nucleus coupled to two ^{1}H and to a methyl group would be expected to be four sets of 1:3:3:1 quartettes. The spectrum was analysed on this basis, assuming that only the middle peaks of the quartettes were resolved and that two of these overlapped at the centre of the spectrum. The coupling constants evaluated were 9.3, 7.2 and 1.7cps., these values agreeing fairly well with those obtained from the ^{1}H spectrum. The averaged values for the coupling constants were: $J^{o}_{F2}=9.4$ [5], $J^{m}_{F1}=7.2$ and $J^{o}_{FMe_1}=1.7$cps.

(D) Carboxylic Ester Derivatives of Fluorobenzene

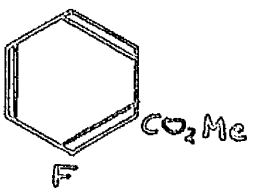
The spectra of these compounds were similar to those of the methyl derivatives in that a full analysis could not be made in every case. Where the spectra have been approximated to first order, the coupling constants and chemical shifts will be subject to some error.

Methyl o-fluorobenzoate(I) had a complex ring proton resonance due to the ABCD part of an ABCDX system. The mid-point of the multiplet was at 2.55τ. The resonance of the methoxy protons was a single peak at 6.12τ. The ^{19}F spectrum consisted of a set of six peaks some of which showed further splitting. The mid-point of the multiplet was at 109.0ppm.

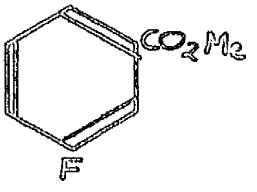
Methyl m-fluorobenzoate(II) had a complicated ring proton signal at 2.49 τ (mid-point). The single peak due to the methoxy-protons occurred at 6.11τ. The ^{19}F spectrum had a complex set of ten peaks, approximately symmetrical about the mid-point at 112.8ppm.

Methyl p-fluorobenzoate(III) showed a spectrum characteristic of an A_2M_2X system. The ring proton resonance consisted of two multiplets, each split into two parts due to AX and MX coupling respectively. In the low field multiplet (A_2) all four strong peaks were well resolved but in the highfield multiplet (M_2) two of the strong peaks were coincident, giving the appearance of a triplet. The value of N (=8.8cps) was readily found from both multiplets and also the values of the ^1H-^{19}F coupling constants (8.4cps. highfield, 5.6cps. lowfield). This enabled the chemical shifts to be assigned to the protons as follows: H_A (ortho to the $-CO_2Me$ group) at 1.99τ, H_M (ortho to the F atom) at 2.96τ. The $-CO_2Me$ proton

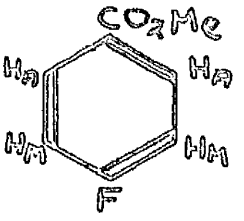
resonance was a single peak at 6.13τ.



(I)



(II)



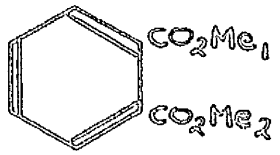
(III)

The ^{19}F resonance, a nine line multiplet, consisted of a 1:2:1 triplet, each peak of which was further split into overlapping 1:2:1 triplets. This type of spectrum is characteristic of the X part of an A_2M_2X system. The coupling constants evaluated were 8.5 and 5.5cps. The average coupling constants obtained for the compound were $J^{o}_{HF}=8.4^{(5)}$, $J^{m}_{HF}=5.5^{(5)}$ and $(J^{o}_{HH} + J^{p}_{HH}) = 8.8$cps.

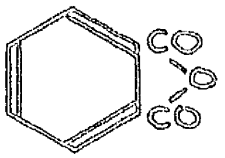
Dimethyl-3-fluoro-phthalate(IV) had a ring proton spectrum of 14 peaks, mid-point at 2.49τ, due to the ABC part of an ABCX system. The resonance due to the methyl protons consisted of two peaks at 6.12 and 6.15τ. By analogy with the methyl resonance in the xylenes the peak at 6.12τ was assigned to Me_1 and the 6.15τ peak to Me_2. The ^{19}F spectrum consisted of two peaks and a group of three peaks equidistant between them, the mid-point of the multiplet being at 115.8ppm.

3-Fluoro-phthalic anhydride(V) showed a complex multiplet ring proton resonance similar to that of (IV) but the mid-point of the multiplet was at 2.24τ. The ^{19}F spectrum showed seven lines, mid-point at 109.2ppm., one of which

was more intense than the others. This was analysed as the X part of an AMPX first order spectrum, assuming that the more intense line was due to two coincident lines. The coupling constants evaluated were: J^{o}_{HF}=7.9, J^{m}_{HF}=4.0, J^{p}_{HF}=1.1cps.



(IV)



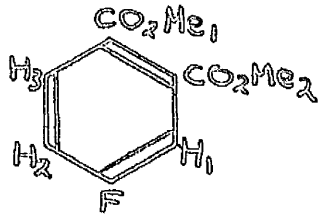
(V)

Dimethyl-4-fluoro phthalate(VI) The ring proton resonance of this compound consisted of a complex multiplet containing seventeen resolved peaks, the mid-point being at 2.60τ. The methyl proton resonance consisted of two partially resolved peaks at 6.16τ (due to Me_1) and 6.18τ (due to Me_2). These assignments were made by comparison with the xylenes. The ^{19}F spectrum was a set of six peaks with the middle two twice as intense as the other four; the multiplet was symmetrical about the mid-point at 109.7ppm. This was analysed as the X part of a first order A_2MX spectrum i.e. a double 1:2:1 triplet. This assumes that both ortho ^{1}H-^{19}F coupling constants are equal. The values obtained were $J^{o}_{F1}=J^{o}_{F2}$=8.4 and J^{m}_{F3}=5.5cps.

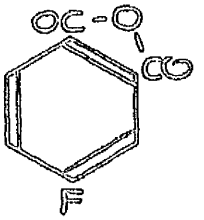
4-Fluoro-phthalic anhydride(VII) showed a ring proton spectrum similar to that of (VI) but the mid-point was

at 2.20 τ. The ^{19}F spectrum consisted of a set of seven peaks, with one peak approximately twice as intense as the other six. The mid-point of the multiplet was at 98.3ppm. This was analysed as the X part of a first order AMPX spectrum assuming that the intense peak was due to two coincident peaks. The analysis gave J^{o}_{HF}=8.0 and 7.2cps., J^{m}_{HF}=4.6cps.

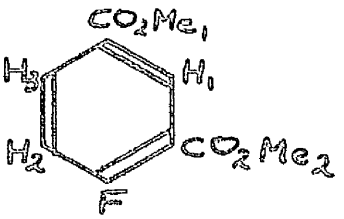
(VI)



(VII)



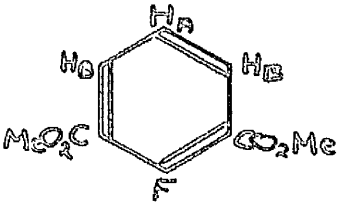
Dimethyl-4-fluoro-isophthalate(VIII) The ring proton resonance consisted of two sets of four peaks at 1.56τ and 2.84τ and a set of eight peaks at 1.87 τ. The relative intensity ratio was 1:1:1. The spectrum was a good approximation to the AMP part of a first order AMPX system. The coupling constants found were J^{o}_{23}=8.5, J^{m}_{13}=2.0, $J^{p}_{12} \sim 0$, J^{o}_{F2}=10.0, J^{m}_{F3}=4.5[5] and J^{m}_{F1}=7.0. From these values, the multiplets were assigned as follows: H_1 at 1.56, H_2 at 2.84 and H_3 at 1.87 τ. The methyl proton resonance was two peaks at 6.07 and 6.10 τ which were assigned to Me_1 and Me_2 respectively.



(VIII)

The ^{19}F resonance was an eight line multiplet characteristic of a first order AMPX system. The chemical shift was 102.7ppm. and the coupling constants obtained were 10.2, 7.0 and 4.7cps. in good agreement with the coupling constants obtained from the ^{1}H spectrum. Averaged values are J^{o}_{F2}=10.1, J^{m}_{F1}=7.0, J^{m}_{F3}=4.6cps.

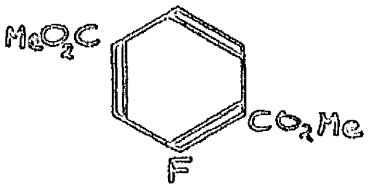
Dimethyl 2-fluoro-isophthalate(IX) The ring proton spectrum showed nine resolved peaks, the mid-point of the multiplet being at 2.40τ. The methyl proton resonance was a single peak at 6.08τ.



(IX)

The ^{19}F resonance showed a 1:2:1 triplet at 106.6ppm. characteristic of the X part of an AB_2X system where J_{AX}=0 (ABRAHAM, BISHOP, RICHARDS 1960). The triplet separation was 6.3cps., giving J^{m}_{FH}=6.3cps.

Dimethyl 2-fluoro-terephthalate(X) showed a ring proton resonance consisting of three peaks that each showed further splitting. The mid-point of the multiplet was at 2.30τ. The resonance due to the methyl protons was a single peak (broadened) at 6.09τ.



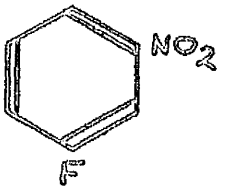
(X)

The ^{19}F resonance showed a multiplet that approximated to the X part of a first order AMPX system, and was analysed as such. Coupling constants obtained were J^{o}_{HF}=10.5, J^{m}_{HF}=5.4, J^{p}_{HF}=1.5cps.

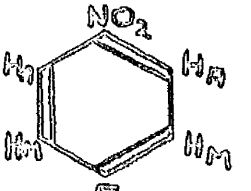
(E) Nitro-Derivatives of Fluorobenzene

m-Nitro-fluorobenzene showed a complex set of peaks, mid-point at 2.35τ, due to the ring proton resonance. The ^{19}F spectrum consisted of a complex multiplet, the mid-point being at 109.7ppm.

p-Nitro-fluorobenzene had a spectrum, similar to that of p-F·$C_6H_4CO_2Me$, characteristic of an A_2M_2X system. The parameters obtained from the ^{1}H spectrum were as follows: H_M at 2.78 and H_A at 1.73τ, J^{o}_{HF}=7.6, J^{m}_{HF}=4.8cps. and J^{o}_{HH} + J^{p}_{HH}=9.3cps. The ^{19}F chemical shift was at 103.2ppm. and the coupling constants obtained were J^{o}_{HF}=7.8, J^{m}_{HF}=4.8cps. The average values for the ^{1}H-^{19}F coupling constants are J^{o}_{HF}=7.7 and J^{m}_{HF}=4.8cps.

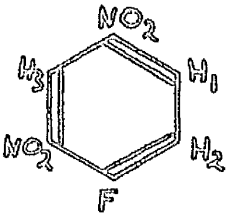


(I)



(II)

2,4 Dinitro-fluorobenzene(III) had a ring proton resonance consisting of a 1:2:1 triplet at 2.30τ, the separation of the peaks being 9.4cps. This was assigned to H_2. The rest of the spectrum consisted of a complex signal, mid-point at 1.22τ, due to H_1 and H_3.



(III)

The ^{19}F spectrum consisted of a seven peak multiplet, symmetrical about the centre peak at 103.2ppm. The central peak was twice as intense as the others and, assuming that this was due to the coincidence of two peaks, the resonance was analysed as being the X part of an ABMX first order spectrum. The coupling constants obtained were 9.7, 6.2 and 3.8cps. The coupling constants for the compound from this approximate solution are therefore J^{o}_{HF}=9.5[5], J^{m}_{HF}=6.2 and 3.8cps.

The proton spectrum of this compound has previously been analysed as an ABMX system (RAO, PUTCHA 1960). The

appearance of the spectrum has been found to be a function of the solvent used, as the chemical shifts of the protons are altered by a change in solvent, although the spectrum is still fitted by an ABMX approximation (SCHAEFER 1962). Recently the spectra of acetone and benzene solutions have been solved using an iterative computor programme and the differences in parameters with solvent change have been confirmed (RAO 1963-4). The relevant parameters are shown in Table III, 9.

Table III, 9

	Pure liquid	Acetone solution	Benzene solution	Present work
J^{o}_{F2}	10.18	10.4	9.69	9.7
J^{m}_{F1}	3.79	3.6	3.63	3.8
J^{m}_{F3}	6.19	6.44	6.45	6.2

Considering the approximations involved in the present work, the agreement is good.

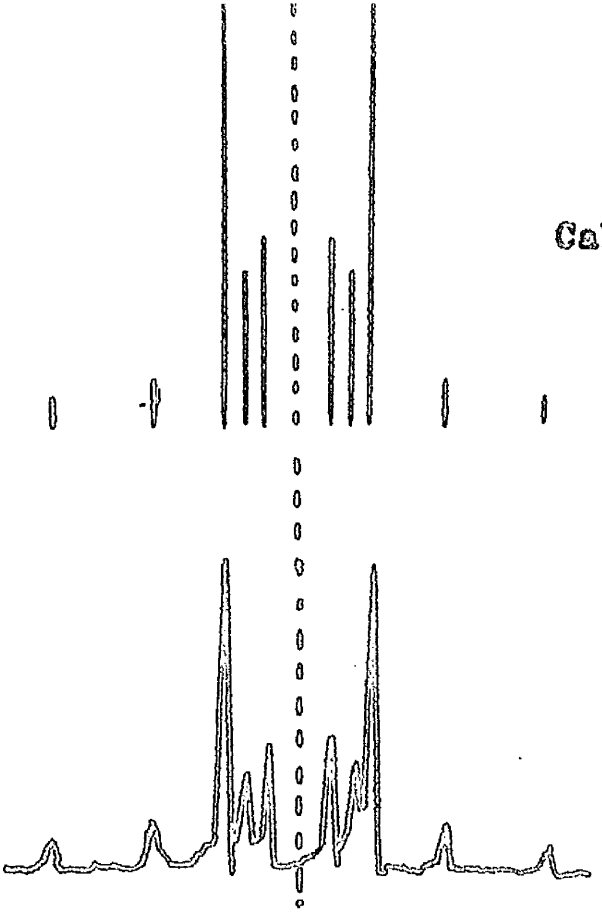


Fig. 3,1

Calculated and experimental multiplets for o-$C_6Cl_2F_4$

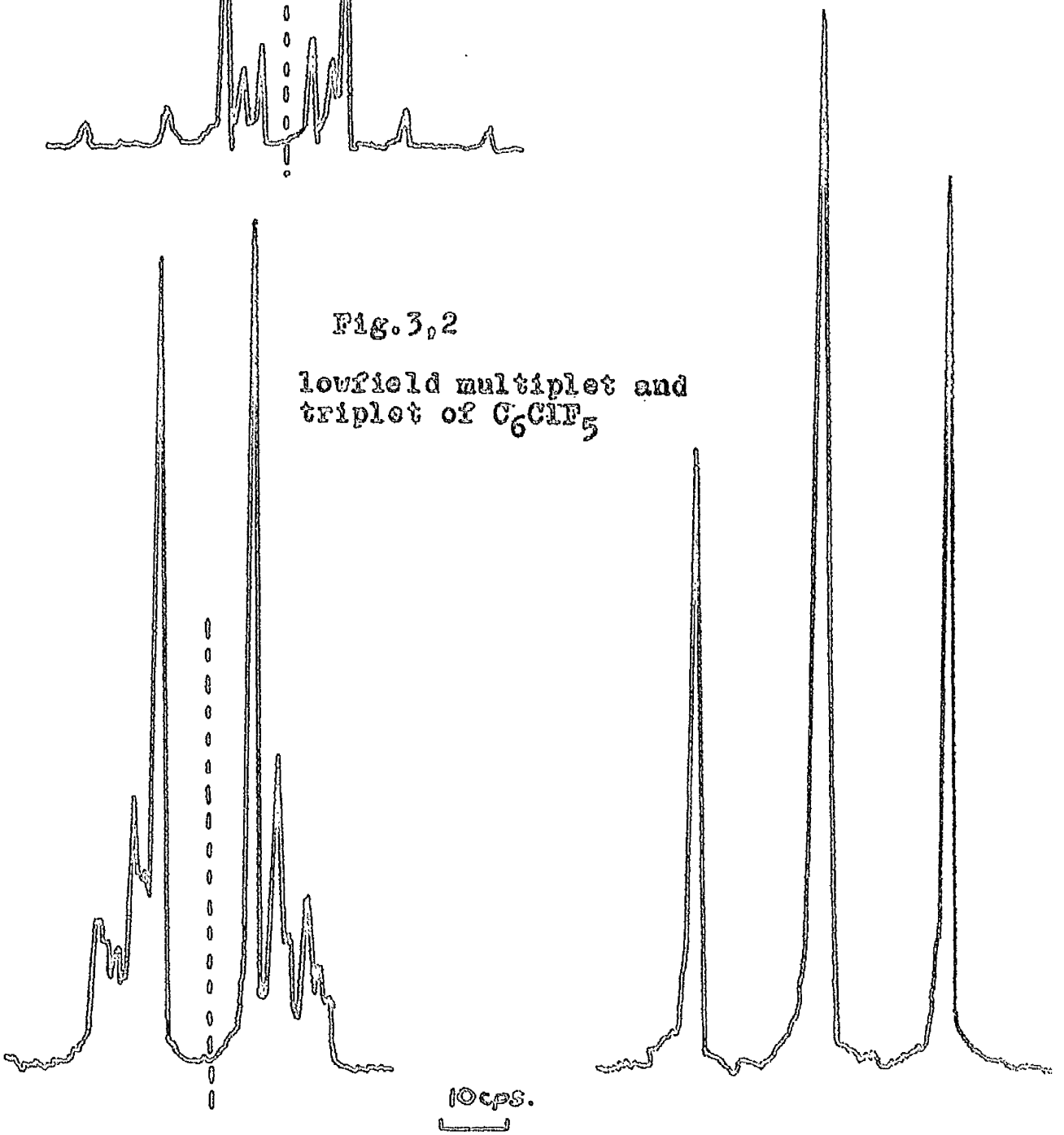


Fig. 3,2

lowfield multiplet and triplet of C_6ClF_5

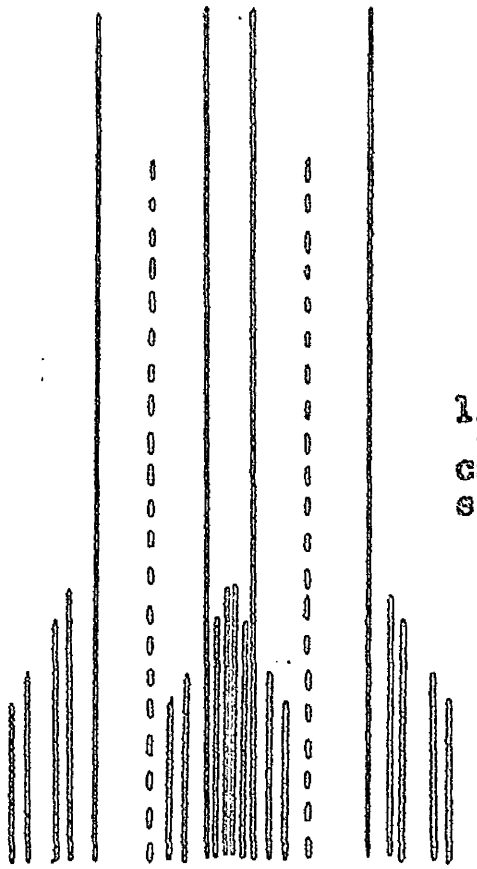
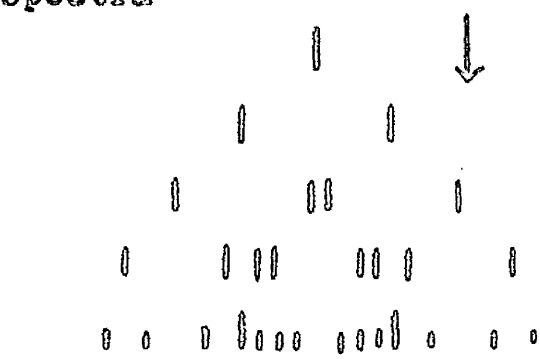
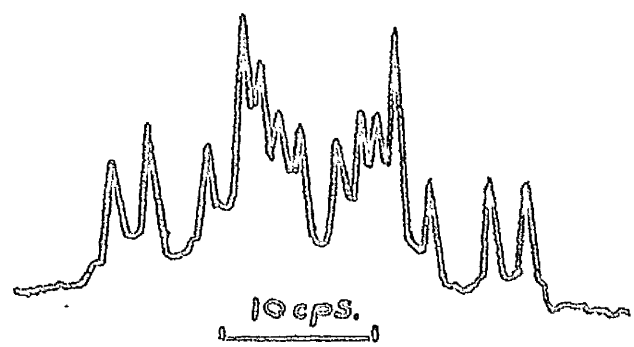


Fig.3,3

^1H resonance of C_6HClF_4 calculated and experimental spectra





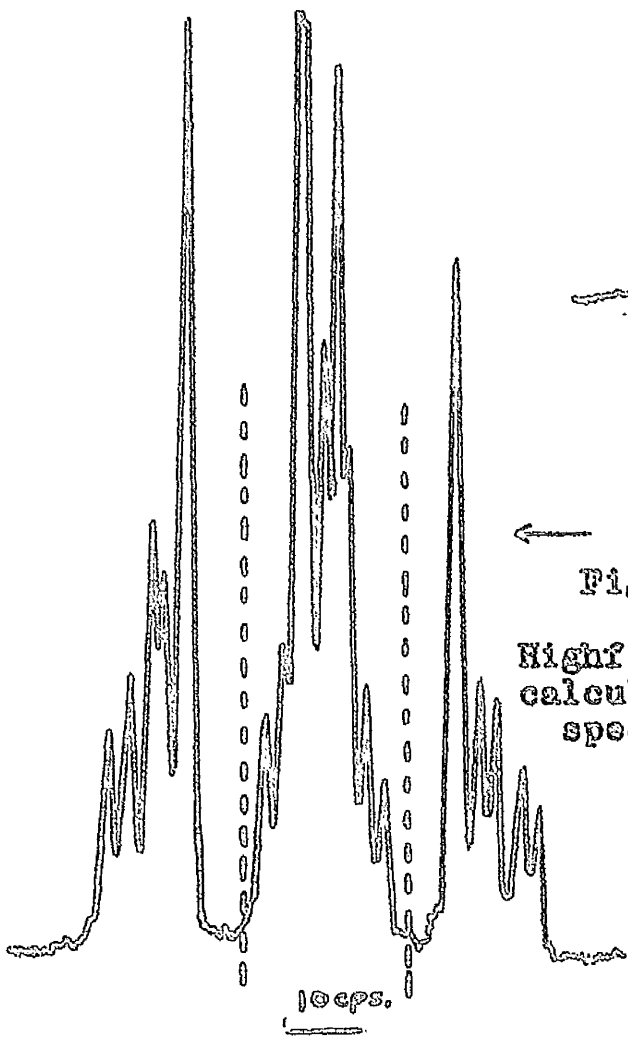
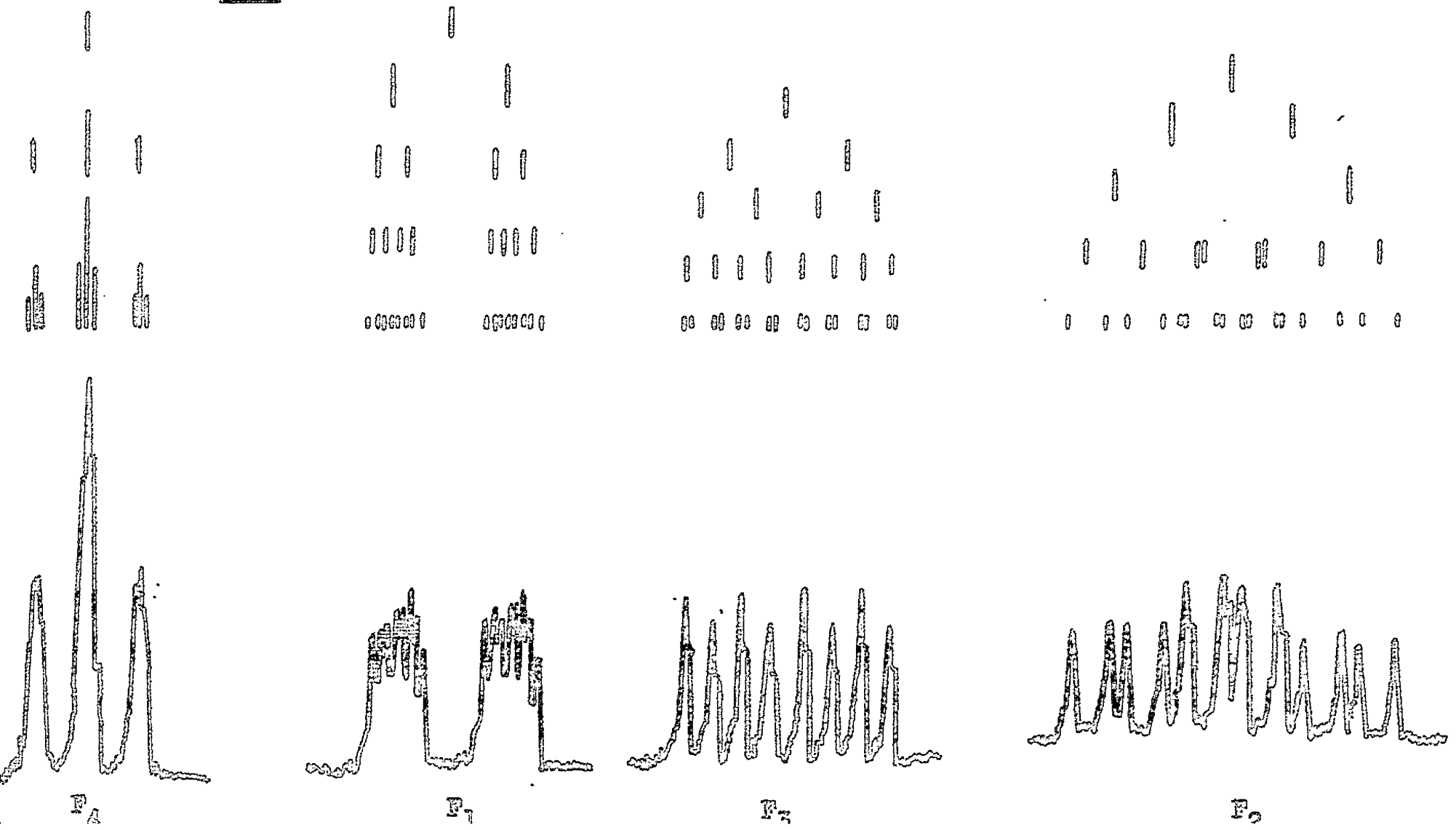


Fig.3,2

Highfield multiplet of C_6ClF_5 calculated and experimental spectra

Fig.3,2 ^{19}F resonance of C_6HClF_4
calculated and experimental multiplets



CHAPTER FOUR

THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME ALIPHATIC FLUOROCARBON DERIVATIVES

Introduction

The majority of aliphatic fluorocarbons are volatile liquids that are very suitable for study by high resolution nuclear magnetic resonance spectroscopy. Generally the shifts between non-equivalent ^{19}F nuclei are large, so the spectra are well defined and the signals can be assigned without difficulty. The magnitudes of ^{19}F-^{19}F coupling constants in various environments and the factors that affect chemical shifts have been widely studied. The structures of aliphatic fluorine compounds can often be deduced from their N.M.R. spectra, by analogy with the spectral parameters of compounds whose structures are known.

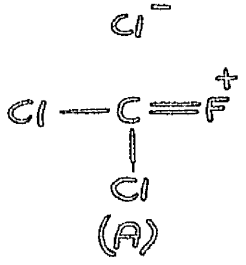
The spectra described in this chapter were examined to determine the structures of the compounds, where these were unknown, and to examine the factors that affect the chemical shifts and coupling constants.

^{19}F Chemical Shifts in Aliphatic Compounds

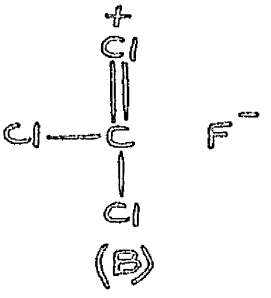
By analogy with the shielding of ^{19}F nuclei in

binary fluorides (referred to in Chs.3 and 5) the shielding of a ^{19}F nucleus in an aliphatic fluorocarbon should be increased when the electronegativity of the atoms bound to the same carbon atom decreases. This has been found to be so in the series of compounds $CH_{4-n}F_n$ (MEYER, GUTOWSKY 1953) and in a number of polyfluoroethanes (ELLEMAN, BROWN, WILLIAMS 1961a). In the series of compounds $CCl_{4-n}F_n$ the reverse is the case (MEYER, GUTOWSKY 1953); the ^{19}F chemical shifts increase in the series $CCl_3F < CCl_2F_2 < CF_3Cl < CF_4$. Examination of the ^{19}F chemical shifts in a number of substituted polyfluoroaliphatic compounds containing up to six carbon atoms (TIERS 1956; MULLER, LAUTERBUR, SVATOS 1957b; SMITH T.S., SMITH E.A. 1959), shows that there is a general relationship between the chemical shift and the environment of the nucleus. In fully fluorinated compounds the shielding of ^{19}F nuclei increases in the order $CF_3 < CF_2 < CF$ which suggests that the amount of charge that a fluorine atom is able to draw from a carbon atom decreases, as the number of fluorines bound to the carbon increases. However, the chemical shifts in $CF_3 \cdot CF_2 \cdot CClFI$ (CRAPO, SEDERHOLM 1960) show that the shielding decreases in the order $CF_2 > CF_3 > CF$. The geminal Cl and I atoms deshield the ^{19}F nucleus to a marked degree. The shielding of the ^{19}F nuclei in a

given group (e.g. $-CF_2-$, $-CFCl-$) increases with an increase in the electronegativitids of the adjacent groups. The 'apparent electron withdraving power' of substituents adjacent to a $-CF_2-$ group is $CCl_3 \sim CH_2I > COCl \sim CH_2Br > CH_2Cl > CF_3 > CH_2F$; the halides show a similar tendency i.e. I > Br > Cl > F. Both these trends are opposite to that expected from electronegativity considerations, except for CF_3 and CH_2F. It has been suggested that these facts are due to C-F π-bonding (SMITH T.S., SMITH E.A. 1959) or to the 'repulsive deshielding' effect of bulky substituents (TIERS 1956). In particular, the deshielding effect of a chlorine atom has been explained on the basis of the greater tendency of fluorine to form partial double bonds with carbon. Structure (A) is more likely than structure (B) and leads to an increase in the paramagnetic shielding



(A)



(B)

term. C-F π-bonding has also been invoked to explain progressive bond shortening in the compounds $CH_{4-n}F_n$, as n increases (PAULING 1942). This would account for the deshielding of the ^{19}F nucleus. However, C-F bond shortening will also result from the fact that the

carbon hybrid atomic orbitals have progressively more 2s character as n increases, due to the withdrawal of carbon 2p electrons by the F atoms (PETERS 1963).

There is less information about chemical shifts in unsaturated systems but the deshielding effect on an olefinic ^{19}F nucleus of a gem Cl atom compared with a gem F atom has been reported (TIERS 1961). In a number of polyfluoropropanes the resonance of the ^{19}F nucleus trans to a $-CF_3$ group occurs at a lower applied field than one cis to this group (SWALEN, REILLY 1961).

^{19}F-^{19}F Spin-spin Coupling in Aliphatic Compounds

Although the magnitudes and relative signs of many ^{19}F-^{19}F coupling constants in aliphatic compounds have been determined experimentally, little progress has been made in the calculation and prediction of their values. A molecular orbital treatment of the coupling constants in C_2F_4 (McCONNELL 1956) indicated that significant contributions to the coupling arise from electron spin and electron orbital interactions with the nuclei. A valence bond treatment of ^{19}F-^{19}F coupling in ethanic and ethylenic molecules (KARPLUS 1959) suggested that the contact mechanism is of primary importance. The magnitude of proton coupling constants in aliphatic compounds generally decreases with an increasing number of bonds between them but this is not so for ^{19}F-^{19}F

coupling. In compounds containing a C_2F_5- group, a near zero value for the vicinal ^{19}F-^{19}F coupling constant has been found (SAIKA, GUTOWSKY 1956; CRAPO, SEDERHOLM 1960), although the coupling constants between ^{19}F nuclei separated by four or five bonds are in the range 16-6cps. The range of vicinal coupling constants in halogen substituted ethanes is as follows (HARRIS, SHEPPARD 1963): XF_2CCF_3, 0-5cps.; $XYFCCF_3$, 4-9cps.; X_2FCCF_2Y, 1-8cps.; and XF_2CCFXY, 13-24cps. The magnitudes of the coupling constants increase as the electronegativity of the substituents decreases, i.e. $I > H > Br > Cl \sim CF_3 > F$.

PETRAKIS and SEDERHOLM (1961) have suggested that the mechanism of ^{19}F-^{19}F coupling is 'through space', by the overlap of orbitals (not necessarily bonding) from the F atoms. The coupling constant increases as the F-F distance decreases (and the overlap of orbitals increases), becoming zero when the F-F distance is greater than 2.72°A (approximately twice the Van der Waals radius of a fluorine atom). In the favoured, staggered, configuration of a perfluoroethyl group the distance between vicinal F atoms is 2.72°A or greater. On this basis the zero coupling constants in C_2F_5- compounds are easily explained. The non-zero vicinal coupling constants of halogensubstituted perfluoroethanes can be explained on this theory as a result of the forcing

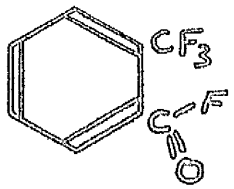
together of vicinal F atoms by the bulky CF_3, Cl or I groups. However, the vicinal ^{19}F-^{19}F coupling constants in HF_2CCF_3 and H_2FCCF_3 are 2.8 and 15.5cps. respectively (ELLEMAN, BROWN, WILLIAMS 1961a) and do not support this theory, as the substituents (H) are smaller than an F atom.

HARRIS and SHEPPARD (1963) have pointed out that in 'through space' ^{19}F-^{19}F coupling, all coupling constants should have the same sign but geminal and vicinal ^{19}F-^{19}F coupling constants are of opposite sign in $BrF_2C{\cdot}CFBr_2$ (MANATT, ELLEMAN 1962). An alternation in sign for the series geminal, vicinal and 1,3 ^{19}F-^{19}F coupling constants has been found to be general in fluoropropanes (EVANS 1962b; EVANS, MANATT, ELLEMAN 1963). This is consistent with a 'through bond' coupling mechanism on a Dirac Vector model (McCONNELL 1955). The vicinal coupling constant usually measured is, in fact, an average value of the gauche and trans vicinal coupling constants of the conformers. Low temperature N.M.R. measurements have enabled the magnitudes of the gauche and trans ^{19}F-^{19}F coupling constants in $ClF_2C{\cdot}CCl_2F$ and $BrF_2C{\cdot}CBrF_2$ to be measured (HARRIS, SHEPPARD 1963); J_{gauche} is greater than J_{trans}. These authors have suggested that the reason for small vicinal coupling constants in perfluoroethyl groups lies partly in the

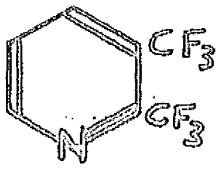
small values of the trans and gauche coupling constants, and partly due to the fact that they are of opposite sign.

Recently NG and SEDERHOLM (1964) have suggested that $^{19}F-^{19}F$ coupling can take place by a 'through bond' or by a 'through space' mechanism. In the 'through bond' mechanism the magnitude of the coupling constant decreases with increasing electronegativity of the other substituents This effect has been demonstrated for geminal $^{19}F-^{19}F$ coupling constants in substituted ethanes (DYER 1963) and for vicinal coupling in substituted ethanes and propanes (NG, SEDERHOLM 1964). This suggests that highly electronegative substituents withdraw electrons from excited triplet or π states of the C-C bond thus reducing the interaction between the nuclei. On this mechanism a zero $^{19}F-^{19}F$ coupling constant would be expected between ^{19}F nuclei separated by more than three bonds.

The 'through space' mechanism is invoked to explain large coupling constants between ^{19}F nuclei separated by at least five bonds but whose electronic clouds are close together. For example, the $^{19}F-^{19}F$ coupling constants in o-trifluoromethylbenzoyl fluoride(C) and in 2,3bis(trifluoromethyl)-pyridine(D) are 10.9 and 12.8cps respectively.



(C)



(D)

Coupling between ^{19}F nuclei, separated by the same number of bonds but where the geometry of the molecule forbids overlap of the electron clouds, is far less; e.g. the 1,4 ^{19}F-^{19}F coupling constant in trans $CF_3ClC{=}CFCF_3$ is 1.3cps. (BEISNER, BROWN, WILLIAMS 1961). Other examples where 'through space' coupling seems plausible will be described later. ^{19}F-^{19}F Coupling constants in unsaturated compounds have not been studied so intensively but a number of empirical relationships have been found to be quite general. These have been of use in assigning the spectra studied in the present work and are described at the end of the chapter.

Discussion of the Spectra Obtained in the Present Work

A. 1,4 Dichlorotetrafluorobuta-1,3-diene Isomers

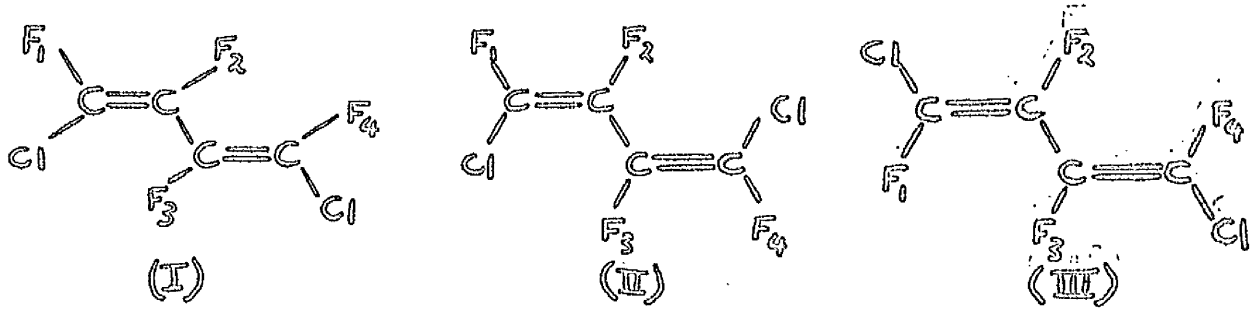
Details of the assignment of the spectra obtained from the cis-trans, cis-cis and trans-trans isomers (I, II and III) are given at the end of the chapter. The resulting chemical shifts and coupling constants are not unbiased but they are self consistent. The coupling constants for the isomers are given in Table IV,1.

Table IV.1

Coupling Constants in $C_4Cl_2F_4$ isomers

Coupling constant	cis-trans isomer		cis-cis isomer		trans-trans isomer	
cis vinylic	11.5	F_1F_2	7.9	F_1F_2, F_2F_4		
trans vinylic	133.8	F_3F_4			$\pm$132.9	F_1F_2, F_3F_4
cis allylic	14.5	F_2F_4			$\mp$ 14.2	F_1F_3, F_2F_4
trans allylic	3.6	F_1F_3	7.9	F_1F_3, F_2F_4		
cis 1,4	5.8^5	F_1F_4				
trans 1,4					27.7	F_1F_4 (a)
trans 2,3	34.1	F_2F_3			34.4	F_2F_3 (a)

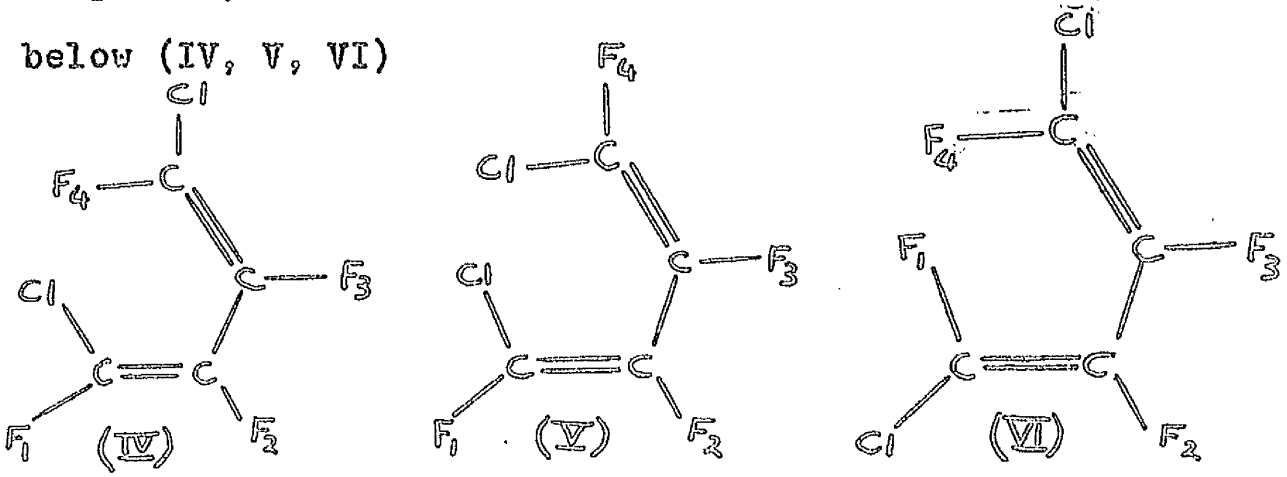
(a) These coupling constants could not be distinguished between from the the spectrum. They were assigned by analogy with the cis-trans isomer.



(I) (II) (III)

The magnitudes of the two 1,4 coupling constants are of interest. The cis 1,4 coupling constant in the cis-trans isomer is of the magnitude expected where the nuclei are separated by two double and three single bonds. (The 1,4 coupling constant in trans $CF_3ClC{=}CFCF_3$ is 1.3cps.). The trans 1,4 coupling constant in the trans-trans isomer is far greater, so there must be an additional contribution to the coupling mechanism.

Assuming that there is free rotation about the C-C single bond, the isomers can exist in the forms shown below (IV, V, VI)



(IV) (V) (VI)

In the trans-trans isomer F_1 and F_4 are fairly close together, so it is plausible to suggest that the F_1F_4 coupling constant results from the contributions of 'through bond' and 'through space' coupling, the latter

being more important. Table IV,2 shows calculated F-Cl, Cl-Cl and F-F inter-nuclear distances for these compounds in the 'cis' form with the appropriate sum of the Van der Waals radii.

Table IV,2

Compound	Halogen-Halogen distance $\overset{\circ}{A}$		Sum of Van der Waals Radii $\overset{\circ}{A}$
trans-trans	F_1-F_4	1.35	2.70 (2F)
cis-trans	F_4-Cl	1.20	3.15 (Cl + F)
cis-cis	Cl-Cl	0.95	3.60 (2Cl)

The halogen-halogen distances were found using the following values for the structural parameters of the isomers; $F\hat{C}Cl=F\hat{C}F=125^{\circ}$, $C\hat{C}C=120^{\circ}$, C-F=1.32, C-Cl=1.70; C=C=1.30; C-C=1.40°A. These are taken from the parameters quoted for chlorofluorethanes and ethylenes (GLOCKER 1950). It was assumed that the molecules are planar and that there is little delocalisation in the carbon bond system. Although the calculated halogen distances are subject to error, it is probable that the relative magnitudes of the distances are correct. Halogen-halogen steric repulsion will decrease in the order Cl,Cl F,Cl F,F, although electrostatic repulsion will be greatest for F,F. On this evidence therefore, it is likely that structures VI and IV will be relatively more important for the trans-trans and cis-trans isomers respectively than structure V will be for the cis-cis isomer. The

large value of the trans 1,4 coupling constant compared to that of the cis 1,4 supports this.

The magnitudes of the coupling constants determined are time-averaged values of the coupling constants in the conformers. There is good agreement between corresponding coupling constants of the cis-trans and trans-trans isomers but discrepancies arise between corresponding coupling constants obtained from the cis-trans and cis-cis isomers. The cis vinylic coupling constant in the cis-cis isomer is 7.9cps., that in the cis-trans isomer is 11.5cps.; the trans allylic coupling constant in the cis-cis isomer is 7.9cps., that in the cis-trans isomer is 3.6cps. Since the magnitudes and signs of coupling constants depend upon the conformation of the molecule (MANATT, ELLEMAN 1962; HARRIS, SHEPPARD 1963), the 'average conformation' at 33.5°C. of the cis-cis and cis-trans isomers must be different.

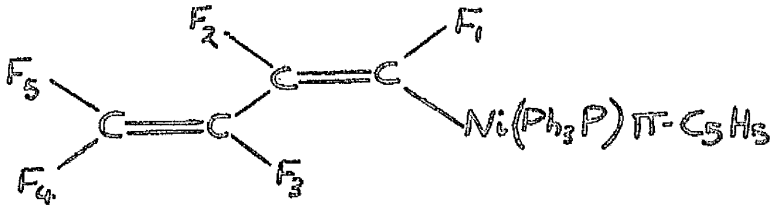
More evidence for the postulate that the preferred conformation of the cis-cis isomer is different from those of the cis-trans and trans-trans isomers, could be obtained from the study of their N.M.R. spectra at low temperatures. Using this technique it has been possible to observe the spectra due to the conformers in substituted fluoroethanes (MANATT, ELLEMAN 1962; HARRIS, SHEPPARD 1963).

The opposite signs of the trans vinylic and cis

allylic coupling constants in the trans-trans isomer, agree with those found for the corresponding coupling constants in fluoropropanes (EVANS, MANATT, ELLEMAN 1963). This suggests that the assumption that cis allylic ^{19}F-^{19}F coupling is greater than trans allylic coupling in polyfluorobutadienes is correct. The spectrum of the cis-trans isomer was assigned on this basis.

The ^{19}F N.M.R. spectrum of π-$C_5H_5 \cdot Ni(Ph_3P) \cdot C_4F_5$ (VII) has been reported recently (McBRIDE, DUDEK, STONE 1964).

(VII)



The structure was assigned from its infra-red and N.M.R. spectra. The 1,4 cis and trans coupling constants (F_1F_5 and F_1F_4) are 7 and 6cps. respectively, in agreement with the cis 1,4 coupling constant obtained here. No 'through space' coupling of F_1 with F_4 and F_5 is possible in this compound. Many of the coupling constants in this compound and those determined in hexafluorobutadiene (DUBOV, TETEL'BAUM, STERLIN 1962) have magnitudes different from the corresponding coupling constants found for the dichlorotetrafluorobutadiene isomers but the relative magnitudes are the same, e.g. trans vinylic > cis vinylic, and cis allylic > trans allylic.

The 1,4 proton coupling constants in butadiene-1,3 and its derivatives are in the range 0—2cps. This is greater than the value expected for protons separated by five bonds (HOBGOOD, GOLDSTEIN 1964) and it has been suggested that delocalisation in the carbon bond chain is responsible for the relatively large values. No evidence was found for such delocalisation in the dichlorotetrafluorobutadiene isomers.

The fluorine nuclei at the 2, and 3 carbon positions are more shielded than those in the 1 and 4 positions. This could be due to the deshielding effect of the 1 and 4 chlorine atoms, although the 2 and 3 positions in hexafluorobutadiene are more shielded than the 1 and 4 (DUBOV, TETEL'BAUM, STERLIN 1962). Table IV,3 gives the chemical shifts obtained.

Table IV,3

^{19}F Chemical Shifts in $C_4Cl_2F_4$ Isomers

Nucleus	Chemical shifts (ppm.)		
	cis-trans	cis-cis	trans-trans
F_1	92.8	91.8	107.6
F_2	140.2	139.3	155.2
F_3	153.2	139.3	155.2
F_4	105.4	91.8	107.6

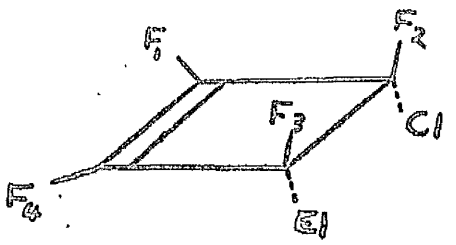
All chemical shifts are positive, relative to CCl_3F.

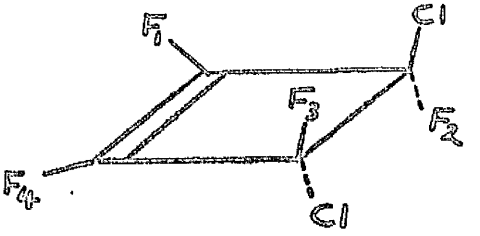
The ^{19}F chemical shifts of nuclei in the 2 and 3 positions are affected by the nature of the vinylic and to a lesser degree, the allylic substituents. Replacement of a trans vinylic F substituent by Cl results in a deshielding of 15.0ppm., when the cis allylic substituent is F and of 13.9ppm., when the cis allylic substituent is Cl. Replacement of a cis allylic F substituent by Cl produces a deshielding of 2.0ppm., when the trans vinylic substituent is F and of 0.9ppm., when the trans vinylic substituent is Cl.

The ^{19}F chemical shifts of nuclei in the 1 and 4 positions are affected by the stereorelationship of the vinylic and allylic F substituents. A ^{19}F nucleus having trans vinylic and cis allylic F substituents is more shielded than one which has cis vinylic and trans allylic F substituents. The differences found are 12.6ppm. where the 1,4 atoms are cis to each other and 15.8ppm., where they are trans. Similar vinylic and allylic effects have been reported for halogenated propenes (SWALEN, REILLY 1961).

B. <u>3,4-Dichlorotetrafluorocyclobutene-1 Isomers</u>

The ^{19}F N.M.R. spectrum showed the presence of a mixture of the diastereomers I and II but did not permit their individual assignment.





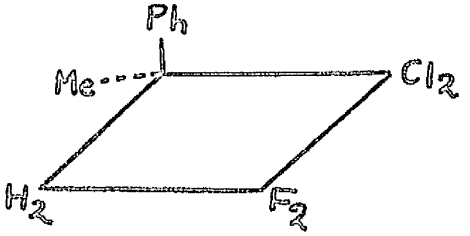
From the spectrum the ^{19}F-^{19}F coupling constants were assigned as follows:

for isomer (I) $\left.\begin{matrix} J_{F_1F_2} \\ J_{F_1F_3} \end{matrix}\right\} = \left\{\begin{matrix} 7.2 \\ 5.3 \end{matrix}\right.$ cps. and

for isomer (II) $\left.\begin{matrix} J_{F_1F_2} \\ J_{F_1F_3} \end{matrix}\right\} = \left\{\begin{matrix} \pm 10.7 \\ \pm 5.1 \end{matrix}\right.$ cps. and $\left.\begin{matrix} J_{F_1F_4} \\ J_{F_2F_3} \end{matrix}\right\} = \left\{\begin{matrix} 4.4 \\ 1.2 \end{matrix}\right.$ cps

The chemical shifts were assigned assuming that the ^{19}F nuclei having a gem Cl substituent (F_2F_3) will be deshielded compared to the olefinic ^{19}F nuclei (F_1F_4). The chemical shifts so obtained are: for isomer (I) F_1F_4 at 135.1 and F_2F_3 at 111.5ppm.; for isomer (II) F_1F_4 at 134.1 and F_2F_3 at 115.4ppm. All resonance occurred upfield from CCl_3F. There is a difference of 3.9ppm. in the shielding of the ethanic ^{19}F nuclei between the syn and anti configurations. Small or zero values for the coupling constants between fluorine atoms attached to neighbouring carbon atoms, have been reported in some tetrafluorocyclobutanes (PHILLIPS 1956). By analogy with this, the 1.2 and 4.4cps. coupling constants in

isomer II are assigned to $J_{F_2F_3}$ and $J_{F_1F_4}$ respectively. It is not possible to distinguish between $J_{F_1F_2}$ and $J_{F_1F_3}$ in either isomer but all four coupling constants are of the same magnitude (5-11cps.). This is unexpected for a 'through bond' coupling mechanism. Anomalous ^1H-^{19}F coupling constants have been reported in some phenyl-substituted-fluoro-cyclobutenes (SHARTS, ROBERTS 1957). The cross ring 1,3 ^1H-^{19}F coupling constant, is greater than the adjacent 1,2 ^1H-^{19}F coupling constant, the respective values being 8-12cps. and 1-2cps. A long range coupling constant (2.1cps.) between one of the ^{19}F nuclei and the methyl group in compound (III) has also been reported (TAKAHASHI, DAVIS, ROBERTS 1962).



(III)

The coupling between 1,2 $-CF_3$ groups in some substituted cyclobutanes has been found to be 10-12cps. when their orientation is cis and zero when their orientation is trans (PROSKOW, SIMMONS, CAIRNS 1963). It has been suggested (NG, SEDERHOLM 1964) that the coupling mechanism in the cis CF_3 case is 'through space'. This cannot occur in the trans CF_3 case and no coupling is observed.

The relatively large values of coupling constants

in cyclic fluorocarbons can be explained on the basis of a 'through space' mechanism, although the distance between 1 and 3 fluorine substituents is rather large for effective overlap. However, the very small coupling between adjacent ^{19}F nuclei cannot be explained by this mechanism.

C. Fluorocarbon Derivatives of Sulphur Hexafluoride

The resonance of the $-SF_5$ group in SF_5X compounds (where X is an alkyl or fluoroalkyl group) is characteristic of an AB_4 system. This indicates that the fluorine atoms have a tetragonal-pyramidal configuration about the sulphur atom, the substituent occupying an apical position in a distorted octahedron (MULLER, LAUTERBUR, SVATOS 1957a). The chemical shifts (ppm. relative to CCl_3F) and coupling constants (cps.) obtained in the present work, together with those of related compounds, are shown in Tables IV,4 and IV,5.

Table IV,4

^{19}F Chemical shifts in perfluoroalkyl derivatives of SF_6

Compound	F_{ax}	F_{eq}	F_1	F_2	F_3	F_4
$SF_5CF_2CF_2Cl$ [a] (1)(2)	-63.1	-45.3	+94.3	+69.9		
$SF_5CF_2CF_3$ [b] (1)(2)	-61.5	-42.0	+100.5	+82.1		
$SF_5CF_2CF_3$ [c] (1)(2)	-61.0	-42.2	+92.0	+81.8		
$SF_5CF_2CF_2CF_2CF_2Cl$ [a] (1)(2)(3)(4)	-62.7	-44.7	+94.2	+121.6	+119.5	+68.4
$SF_5CF_2CF_2CF_2CF_3$ [b] (1)(2)(3)(4)	-60.4	-43.0	+94.3	+122.7	+125.2	+81.5
$SF_5CF_2CF_2CF_2CF_3$ [c] (1)(2)(3)(4)	-61.0	-42.2	+94.5	⟵ +123.0 ⟶		+81.7
SF_6	-57.4					

(a) present work.
(b) ROGERS, GRAHAM (1962).
(c) MULLER, LAUTERBUR, SVATOS (1957a).

Table IV.5

^{19}F-^{19}F Coupling constants in perfluoroalkyl derivatives of SF_6

Compound	FSF_4	$FSCF_2$	SF_4CF_2	SF_4CCF_2	CF_2CF_2	CF_2CCF_2	CF_2CF_2Cl (c)	CF_2CCF_2Cl (c)
$SF_5CF_2CF_2Cl$ [a]	147	5.3	15.0	10.9			1.5	
(1)(2)	$F_{ax}F_{eq}$	F_1F_{ax}	F_1F_{eq}	F_2F_{eq}			F_1F_2	
$SF_5CF_2CF_3$ [b]	152.19	4.82	14.36	8.56			~0	
(1)(2)	$F_{ax}F_{eq}$	F_1F_{ax}	F_1F_{eq}	F_2F_{eq}			F_1F_2	
$SF_5CF_2CF_2CF_2CF_2Cl$ [a]	144	5~8	16	~13	~2	16~19	2.5	14.3
(1)(2)(3)(4)	$F_{ax}F_{eq}$	F_1F_{ax}	F_1F_{eq}	F_2F_{eq}	F_1F_2, F_2F_3	F_1F_3	F_3F_4	F_2F_4
$SF_5CF_2CF_2CF_2CF_3$ [b]	145.96	2.47 [e] / 4.93	17.0	8~9	2.42 [d]		~0	10.80
(1)(2)(3)(4)	$F_{ax}F_{eq}$	F_1F_{ax}	F_1F_{eq}	F_2F_{eq}	F_1F_4		F_3F_4	F_2F_4

(a) present work.
(b) ROGERS, GRAHAM (1962).
(c) these columns include $CF_3 \cdot CF_2$ and $CF_3 \cdot C \cdot CF_2 \cdot$ coupling constants.
(d) this value is for the $CF_3 \cdot C \cdot C \cdot CF_2 \cdot$ coupling constant.
(e) two values reported.

The chemical shifts of the axial ^{19}F nuclei occur at lower field than do those of the equatorial nuclei. The greater shielding of F_{eq} compared to SF_6 is what would be expected when an F atom in SF_6 is replaced by a less electronegative fluorocarbon group. (SAIKA, SLICHTER 1954). When the substituent is an alkyl group (BODEN, EMSLEY, FEENEY, SUTCLIFFE 1963) or an oxygen containing substituent e.g. CF_3O- or $=SO_4$ (MERRILL, WILLIAMSON, CADY, EGGERS 1962) both axial and equatorial ^{19}F nuclei are less shielded than SF_6.

F_{ax} and F_{eq} are less shielded when the fluorocarbon group contains a chlorine atom, compared with the corresponding fully fluorinated compound. The presence of the chlorine atom also accounts for the deshielding of ^{19}F nuclei in the $-CF_2Cl$ group compared to those in the $-CF_3$ group.

Comparison of the chemical shifts in corresponding compounds (e.g. $SF_5CF_2CF_3$ and $SF_5CF_2CF_2Cl$) shows that they can be correlated with the electronegativity of the neighbouring groups in the fluorocarbon chain. An increase in 'neighbouring group electronegativity' produces an increase in the shielding experienced by an ^{19}F nucleus. Hence the chemical shift of a $-CF_2-$ group α to a CF_3- is greater than that of one α to a $-CF_2Cl$ group.

It appears that F_{ax} interacts only with the α ^{19}F nuclei of the fluorocarbon group, although coupling between F_{eq} and the α and β ^{19}F nuclei was observed. This agrees with previous work (MERRILL, WILLIAMSON, CADY, EGGERS 1962; ROGERS, GRAHAM 1962). Coupling invdwing F_{ax} has been observed only with ^{19}F nuclei attached to an α-carbon atom but F_{eq} -α-proton and F_{eq}-OR_f couplings are well known (BODEN, EMSLEY, FEENEY, SUTCLIFFE 1963; MERRILL, WILLIAMSON, CADY, EGGERS 1962). It has been shown that the $-SF_4-$ group screens F_{ax} from the π-aromatic system, in compounds of the type $XC_6H_4SF_5$ (EATON, SHEPPARD 1963) and it seems likely that a similar effect operates here.

The magnitudes of the coupling constants in the fluorocarbon groups are similar to those reported for corresponding nuclei in other fluorocarbons. The greater values of the (1,2), (3,4) and (2,4) coupling constants in the chloropolyfluoro group, compared to those in the perfluoro group canbe explained on the basis of the smaller size and greater electronegativity of fluorine compared to chlorine. The small values of vicinal ^{19}F-^{19}F coupling constants compared to those for 1,3 coupling have already been discussed.

Conclusion

N.M.R. spectroscopy is a very useful means of

determining the structures of aliphatic fluorocarbon compounds, particularly when spectral parameters for analogous compounds are known. The factors that effect chemical shifts and coupling constants are many and no single treatment is universally applicable. However, the chemical shift of a ^{19}F nucleus depends upon the electronegativities of the other atoms in the same group and upon the electronegativities of neighbouring groups. The magnitudes of ^{19}F-^{19}F coupling constants have been explained in terms of both 'through bond' and 'through space' mechanisms but neither of these explanations is definitive. However, the electronegativity and size of substituent and the nature of the bonding in the carbon chain seem to be important.

EXPERIMENTAL

The compounds whose spectra are described in this chapter were all gifts from Imperial Chemical Industries Ltd., Alkali Division. The spectra of the dichlorotetrafluorobutadiene isomers were obtained from 30% solutions in carbon tetrachloride and were referenced internally to CCl_3F. The spectrum of the dichlorotetrafluorocyclobutene isomers was obtained from the neat liquid, the sample being sealed in the N.M.R. tube as it was very volatile. The spectrum was referenced externally to CCl_3F, using $PhCF_3$ as a secondary reference. The $-SF_5$ spectra were obtained from neat liquids and were referenced internally to CCl_3F.

The methods used for obtaining and measuring the spectra have been described in Ch.3. The errors in the chemical shifts and coupling constants are the same as those in the aromatic compounds, except for the $-SF_5$ compounds, where the method of analysis introduced larger errors.

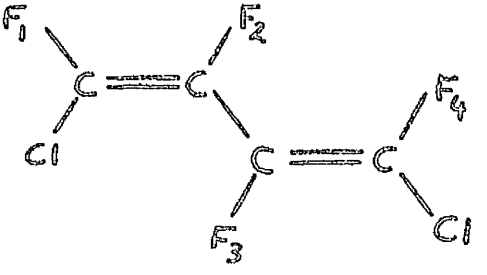
DESCRIPTION OF THE SPECTRA AND THEIR ASSIGNMENT

A. 1,4 Dichlorotetrafluorobutadiene Isomers

The spectra described here are those of three vapour phase chromatographic fractions of a liquid, of molecular formula $C_4Cl_2F_4$. This liquid was the product from the following series of reactions (ROBERTS 1964) $2CClF{=}CClF \Rightarrow CClF{=}CF{-}CClF{-}CCl_2F \xrightarrow{-Cl_2}$ $CClF{=}CF{-}CF{=}CClF$. The N.M.R. spectra of the fractions were consistent with the fact that the product, $C_4Cl_2F_4$, contained the three possible stereo isomers, cis-cis, cis-trans and trans-trans.

Cis-trans-1,4-dichloro-tetrafluoro-1,3-butadiene(I)

This structure was assigned to the fraction, whose N.M.R. spectrum contained four multiplets, each consisting of eight lines of equal intensity. This is characteristic of an AMPX first order spectrum. Both the cis-cis and trans-trans isomers would have spectra characteristic of $A_2B_2(A_2X_2)$ systems.



(I)

Table IV.6

Parameters obtained from the cis-trans spectrum

Chemical Shift[(a)] ppm.	Coupling constants[(b)] cps.	Chemical Shift ppm.	Coupling Constant cps.
9.28	3.53	140.2	11.42
	5.81		14.61
	11.56		32.54
105.4	5.88	153.2	3.70
	14.47		35.61
	133.07		134.60

(a) Chemical Shifts are relative to CCl_3F (internal) and are positive in all cases.

(b) Coupling constants are accurate to $\pm$0.2cps.

The chemical shifts and coupling constants contained from each multiplet are given in Table IV,6.

Using Valence Bond theory to calculate the magnitude of spin-spin coupling constants in ethanic and ethylenic molecules KARPLUS (1959) has shown that the magnitude of trans vinyl F-F coupling is greater than that of cis vinyl F-F coupling. This has been found experimentally in a number of cis and trans phenyl perfluoroalkenes (ANDREADES 1962) and in a number of halogenated propenes (SWALEN, REILLY 1961). In each case the structures of the compounds investigated have been confirmed by other methods. The difference between cis and trans vinyl ^{19}F-^{19}F coupling has been noted often in the literature and the constancy of the trans ^{19}F-^{19}F value ($\sim$120cps.) commented upon (e.g. McCONNELL, REILLY, McLEAN 1956).

In the spectrum of cis-trans $C_4Cl_2F_4$ the largest coupling constant was assigned to the trans vinyl coupling constant $J_{F_3F_4}$. This fixes the cis coupling constant as that common to the other two multiplets and leads to the following partial assignment (Table IV,7). On this evidence there are two possible assignments of the spectrum that will give consistent results.

It has been found to be quite general in substituted fluoroalkenes that cis CF_3:F coupling is greater than trans CF_3:F (ANDREADES 1962; TIERS 1962). The

Table IV.7

Partial assignment of spectrum

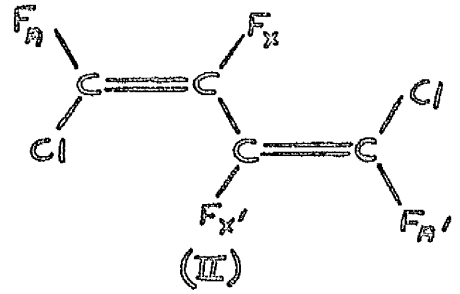
Chemical shifts (ppm.)	(a) Coupling constant(cps.)	Assignment	Chemical shifts(ppm.)	(a) Coupling constant(cps.)	Assignment
92.8	3.6	F_1F_3 or F_2F_4	140.2	11.5	F_1F_2
F_1 or F_2	5.8^5	F_1F_4 or F_2F_3	F_2 or F_1	14.5	F_2F_4 or F_1F_3
	11.5	F_1F_2		34.1	F_2F_3 or F_1F_4
105.4	5.8^5	F_1F_4 or F_2F_3	153.2	3.6	F_1F_3 or F_2F_4
F_4 or F_3	14.5	F_2F_4 or F_1F_3	F_3 or F_4	34.1	F_2F_3 or F_1F_4
	133.8	F_3F_4		133.8	F_3F_4

(a) Averaged values of the coupling constants.

magnitudes of the coupling constants are ~25 and ~10cps. respectively. Assuming that this relationship also holds for butadiene systems, i.e. that $J_{F_2F_4} > J_{F_1F_3}$, an unambiguous assignment is possible. This is as follows: Chemical shifts: F_1 at 92.8, F_2 at 140.2, F_3 at 153.2 and F_4 at 105.4ppm. Coupling constants J_{12}=11.5, J_{13}=3.6, J_{14}=5.8[5], J_{23}=34.1, J_{24}=14.5, and J_{34}=133.8cps.

Cis-cis-1,4 dichloro-tetrafluoro 1,3 butadiene(II)

The spectrum of the second fraction contained peaks due to the cis-trans isomer and two 1:2:1 triplets. The latter were assigned to the cis-cis isomer as the triplets showed no splitting characteristic of trans vinylic ^{19}F-^{19}F coupling.

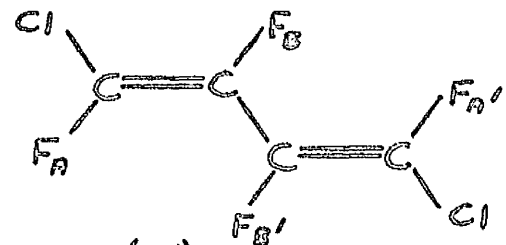


(II)

The spectrum was characteristic of an A_2X_2 system in which K=L=M=0 (GRANT, HIRST, GUTOWSKY 1963). The nomenclature has been described in Ch.3. The value of N obtained was 15.73cps. so $J_{AX} = J_{AX'}$ = 7.9cps. The chemical shifts were assigned by analogy with the cis-trans isomer and are as follows: $F_AF_{A'}$ at 91.8 and $F_XF_{X'}$ at 139.3ppm.

Trans-trans-1,4-dichloro-tetrafluoro-1,3-butadiene(III)

The spectrum of the third fraction consisted of two twelve line multiplets and was assigned to the trans-trans isomer (III).



(III)

The spectrum was symmetrical about its mid-point and each multiplet was approximately symmetrical about its mid-point. The peak intensities of the centre halves of the multiplets were greater than those of the corresponding peaks in the outer halves. This spectrum is characteristic of an A_2B_2 system and was analysed as such. However, the value of K could not be obtained from an A_2B_2 analysis so the spectrum was approximated to an A_2X_2 system to obtain K. A comparison of the parameters obtained from the two analyses is shown in Table IV,8.

Table IV.8

Comparison of spectral parameters from from A_2B_2 and A_2X_2 analyses

Parameter	Value for A_2B_2 Analysis (cps.)	Value for A_2X_2 Analysis (cps.)
$\nu\delta$	1795	1798
N	118.7	118.6
L	147.0	147.1
M	11.85	11.69
K	-	57.15

$\nu\delta$ (cps.) is the difference between the resonance frequencies of the BB′ and AA′ nuclei.

The A_2X_2 approximation holds well for this spectrum, as expected, for the ratio $J/\nu\delta = 0.067$. The coupling constants obtained from the analysis are

$$\left.\begin{matrix} J \\ J' \end{matrix}\right\} = \begin{cases} \pm 132.9 \\ \mp 14.2 \end{cases} \quad \text{and} \quad \left.\begin{matrix} J_A \\ J_B \end{matrix}\right\} = \begin{cases} 34.4 \\ 27.7 \end{cases} \text{ cps.}$$

J and J′ were assigned, using the fact that the trans vinyl ^{19}F-^{19}F coupling constant should be the largest in the system. The coupling constants are

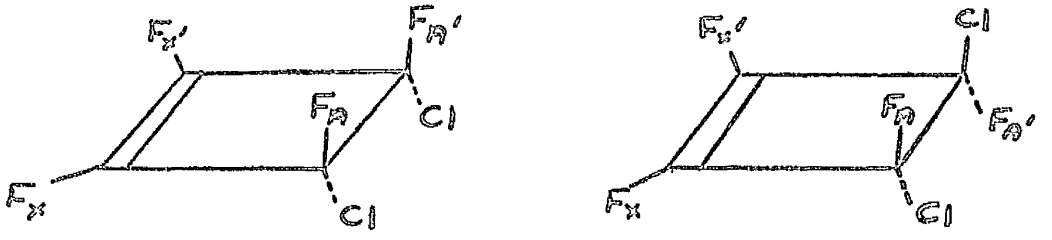
$J_{AB} = \pm 132.9$, $J_{AB'} = \mp 14.2$, $\left.\begin{matrix} J_{AA'} \\ J_{BB'} \end{matrix}\right\} = \begin{cases} 34.4 \\ 27.7 \end{cases}$ cps. The chemical shifts of the nuclei were assigned by analogy with the cis-trans isomer and are $F_AF_{A'}$ at 107.6 and $F_BF_{B'}$ at 155.2ppm.

An attempt to distinguish between K and M by

calculating the peak intensities was unsuccessful as the approximation of the spectrum to A_2X_2 is too good. A calculated A_2X_2 multiplet is shown, together with the lowfield multiplet obtained experimentally, in Fig.4.1.

B. <u>3,4-Dichlorotetrafluorocyclobutene-1 Isomers</u>

The ^{19}F N.M.R. spectrum of a liquid (b.p. 66.5°C.) known to be 3,4-dichlorotetrafluorocyclobutene-1 showed the presence of two isomers I and II in the ratio 60:40. The two possible isomers are



The spectrum of isomer I consisted of two identical multiplets each containing four peaks, symmetrical about the mid-point of the multiplet. This was analysed as an A_2X_2 spectrum where K=M=0. The two doublet separations give values for N and L; from these, the values of J and J' obtained were 7.2 and 5.3cps. These are the values of the coupling constants F_AF_X and $F_AF_{X'}$ but they cannot be distinguished from each other. The value of $J/\nu_0\delta$ was 0.008. The low field multiplet was slightly broadened compared to the high field multiplet. The chemical shifts are tentatively assigned as follows:

$F_AF_{A'}$ at 111.5ppm. and $F_XF_{X'}$ at 135.1ppm.

Isomer II had a spectrum that consisted of two identical multiplets, each symmetrical about its mid-point, although not all the peaks were well resolved. The spectrum was analysed as an A_2X_2 system and the following coupling constants were obtained:

$$J = \pm 10.7; \quad J' = \pm 5.1, \quad \left.\begin{matrix} J_A \\ J_X \end{matrix}\right\} = \left\{\begin{matrix} 4.4 \\ 1.2 \end{matrix}\right. \text{ cps.}$$

The chemical shifts are tentatively assigned as follows: $F_AF_{A'}$ at 115.4 and $F_XF_{X'}$ at 134.1ppm. The ratio $J/\Delta\delta = 0.015$. It was not possible to assign the multiplets to particular isomers from the spectral parameters. The experimental and calculated spectra of the two isomers are shown in Fig.4,2.

C. Fluorocarbon derivatives of Sulphur Hexafluoride

Analysis of the spectra of $-SF_5$ compounds

The spectrum arising from this type of compound consists of an AB_4 system due to the $-SF_5$ group and a set of multiplets arising from the fluorocarbon chain. The chemical shift between the two resonances is very large so both parts of the spectrum are easily recognised. Methods for the analysis of AB_4 systems have been reported by several authors (e.g. CORIO 1960; CHAPMAN, HARRIS 1963) based on the evaluation of the Hamiltonian

for the system. Explicit functions for the transition frequencies of an AB_4 system and their relative intensities have been given (BODEN, EMSLEY, FEENEY, SUTCLIFFE 1963). The spectrum consists of nine resonances due to A and a 'doublet', each part of which is split into six peaks, due to B_4. The method used for analysing the $-SF_5$ resonance in the present work was a graphical solution due to MERRILL, WILLIAMSON, CADY and EGGERS (1962). These authors have computed the theoretical spectra of AB_4 systems for various values of the ratio $J/\nu\delta$, using the value J = 150cps. J(cps.) is the coupling constant between A and B_4 and $\nu\delta$ (cps.) the chemical shift between A and B_4. The 21 transition frequencies are numbered such that when all the lines are well resolved (at about $J/\nu\delta$=0.25), the extreme line of A is 1, the other lines being numbered in order going towards B_4. If the transition frequencies are measured relative to the centre of the B_4 resonance, line 6, the centre of the A resonance, gives the value of $\nu\delta$ directly. The pairs of lines 14,16; 12,17; 11,18 and 10,19 are symmetrically positioned about the zero point. The ratio $R = \frac{(8)-(10)}{(6)-(10)}$ (where (6), (8) and (10) represent the line frequencies) is a sensitive function of the value of $J/\nu\delta$. If the values of lines 6,8, and 10 are readily obtained from the spectrum, the value of $J/\nu\delta$ can be

read off from a graph of R against $J/\nu_0\delta$. This graph is obtained using the computed spectral data.

In the present work the $-SF_5$ spectra were complicated by further splitting of the 21 peaks due to coupling with the fluorocarbon nuclei. This made the accurate determination of the position of line 10 impossible, so its position was estimated. The unperturbed resonance frequency of B_4 was taken to be the mid-point of the strongest peaks in each half of the B_4 'doublet' which were assumed to be the positions of (11) and (18). The values of the chemical shift and the coupling constant between A and B_4 were determined as already described and the theoretical positions of the lines calculated. This was done by obtaining the line positions from graphs of the position versus $J/\nu_0\delta$. Graphs of the 21 line position for different values of $J/\nu_0\delta$ were drawn using the computed spectral data (Document 7066, ADI Auxiliary Publication Project, Library of Congress, Washington). These line positions (multiplied by J/150) were found to agree fairly well with the experimental values. The spectra due to the fluorocarbon groups were analysed as first order systems but all the coupling constants could not be evaluated when the group contained more than two carbon atoms. The spectra were broadened, due ~~to the quadrupole relaxation effect of the ^{33}S nucleus~~

(~~GILLESPIE, QUAIL 1963) and~~ to the fact that many of the coupling constants are of the same order of magnitude.

ω-Chloropolyfluoroethyl-sulphur pentafluoride(I)

The resonance due to the $-SF_5$ group consisted of nine peaks due to the axial fluorine atom, each split into 1:2:1 triplets by the $<-CF_2$ group and two sets of complex peaks, due to the four equatorial fluorine atoms. The B_4 signal contained more than 12 peaks due to coupling with the fluorocarbon side chain.

$$F\text{-}SF_4\text{-}CF_2\text{-}CF_2\text{-}Cl$$
$$F_{ax}\ F_{eq}\ (1)\ (2)$$

(I)

Analysis of the $-SF_5$ spectrum gave the following parameters: chemical shifts F_{ax} at -63.1ppm. (from CCl_3F) and F_{eq} at -45.3ppm; coupling constants $J_{F_{ax}F_{eq}} = 147$, and $J_{F_{ax}F_1} = 5.3$cps. Table IV,9 compares the line frequencies (in cps. relative to the resonance frequency of B_4) measured from the spectrum, with those determined from the graphs for $J/\nu_o\delta = 0.219$.

The fluorocarbon spectrum consisted of two 1:4:6:4:1 quintettes, each peak being further sphit, at +69.9ppm. (due to F_2) and at+94.3ppm. (due to F_1). The multiplets were assigned on the basis that the magnitude of $SF_5\text{-}(CF_2)_n\text{-}$ coupling decreases with increasing bond

Table IV.9

Comparison of experimental with calculated line frequencies

Line No.	Position measured from spectrum (cps. relative to B_4)	Position calculated from graphs (cps. relative to B_4)	Line No.	Position measured from spectrum (cps. relative to B_4)	Position calculated from graphs (cps. relative to B_4)
1.	-982	-987	7.	-616	-612
2.	-878	-867	8.	-542	-538
3.	-828	-827	9.	-422	-422
4.	-758	-755	10.	- 88	-80
5.	-700	-706	11.	- 74	-70
6.	-670	-662	18.	+ 74	+70

The experimental and calculated $-SF_5$ spectra are shown in Fig.4,3

distance. The quintette splitting in the highfield multiplet was 15.0cps. and in the low field 10.9cps., giving $J_{F_1F_{eq}}$ = 15.0 and $J_{F_2F_{eq}}$ = 10.9cps. Each peak of the highfield quintette was split into six peaks. These were well resolved and were analysed as a double triplet giving $J_{F_1F_{ax}}$ = 5.2 and $J_{F_1F_2}$ = 1.5cps. Each peak of the lowfield quintette was split into a triplet confirming $J_{F_1F_2}$ = 1.5cps.

<u>δ-Chloropolyfluoro-n-butyl-sulphur pentafluoride(II)</u>

The resonance due to the axial fluorine atom (A) consisted of nine peaks, each split into triplets. The equatorial fluorine resonance (B_4) consisted of two sets of peaks, each set having more than six peaks due to coupling with the perfluorobutyl group.

$$F\text{-}SF_4\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}Cl$$
$$F_{ax}\ F_{eq}\ (1)\ (2)\ (3)\ (4)$$
(II)

The analysis of the $-SF_5$ spectrum gave F_{ax} at -62.7, F_{eq} at -44.7ppm. and $J_{Fax.Feq}$ = 144cps. The triplet separation in A gave $J_{F_1F_{ax}}$ = 5.1cps. Table IV,10 compares the experimental line frequencies with those obtained from the graphs using $J/\nu\delta$=0.212.

That part of the spectrum due to the fluorocarbon group consisted of four multiplets. These were analysed as first order spectra but due to the poor resolution of the fine structure in the multiplets, the coupling

Table IV.10

Comparison of experimental with calculated line frequencies

Line No.	Position measured from spectrum (cps relative to B_4)	Position calculated from graphs (cps. relative to B_4)	Line No.	Position measured from spectrum (cps relative to B_4)	Position calculated from graphs (cps. relative to B_4)
1.	-992	-989	7.	-625	-620
2.	-889	-874	8.	-552	-554
3.	-838	-831	9.	-433	-430
4.	-768	-763	10.	-81	-79
5.	-711	-714	11.	-66	-69
6.	-680	-670	18.	+66	+69

The experimental and calculated $-SF_5$ spectra are shown in Fig.4.4.

constants obtained are subject to error ($\backsim$3-4cps.). The multiplet at lowfield (chemical shift +68.4ppm.) was a 1:2:1 triplet each peak of which was split into three peaks. This was assigned to F_4, by analogy with $SF_5CF_2CF_2Cl$ and because there was no evidence for coupling with the $-SF_5$ group. The coupling constants obtained were $J_{F_3F_4}$ = 2.5 and $J_{F_2F_4}$ =14.3cps., the assignment being made by analogy with the coupling constants in compounds containing $CF_3 \cdot CF_2 \cdot CF_2-$ groups (ELLEMAN, BROWN, WILLIAMS 1961b). A broad septette of peaks, at +94.2ppm., each peak of which was split into six peaks, was assigned to F_1, by analogy with $SF_5CF_3CF_3Cl$ and because this multiplet contained the largest septette splitting. The smaller splittings were analysed as double triplets. This gave the following coupling constants: $J_{F_1F_{eq}} = J_{F_1F_3} = 16$, $J_{F_1F_{ax}} = 8$ and $J_{F_1F_2} = 2$cps.

The resonance due to F_2 and F_3 appeared at high field. The multiplets were very broad and were probably not true first order spectra. The resonance at +121.6ppm. was a broad septette, the peak separation being $\sim$13cps. This was assigned to F_2, on the basis of the septette splitting, giving $J_{F_2F_{eq}} = J_{F_2F_4} = \sim$13cps. The values of the coupling constants $J_{F_2F_3}$ and $J_{F_1F_2}$ could not be determined from this multiplet but they must be small

(~2cps.) to account for the peak widths. The multiplet at +119.5 was assigned to F_3. It consisted of a 1:2:1 broad triplet, the outer peaks of which were split into three peaks; the centre peak was a broad doublet. The large triplet splitting is 19cps., giving $J_{F_1F_3}$ = 19cps. Values for $J_{F_3F_4}$ and $J_{F_2F_3}$ could not be obtained, nor was any evidence found for coupling between F_3 and F_{eq}.

Although all the coupling constants in the molecule were not obtained, those that were enabled a self consistent assignment to be made. The values of the coupling constants are as follows: $J_{F_3F_4}$ = 2.5, $J_{F_2F_4}$ = 14.3, $J_{F_1F_3}$ = 16~19, $J_{F_2F_{eq}}$ = ~13, $J_{F_1F_2}$ = ~2, $J_{F_1F_{eq}}$ = 16, $J_{F_1F_{ax}}$ = 5~8 and $J_{F_{eq}F_{ax}}$ = 144cps.

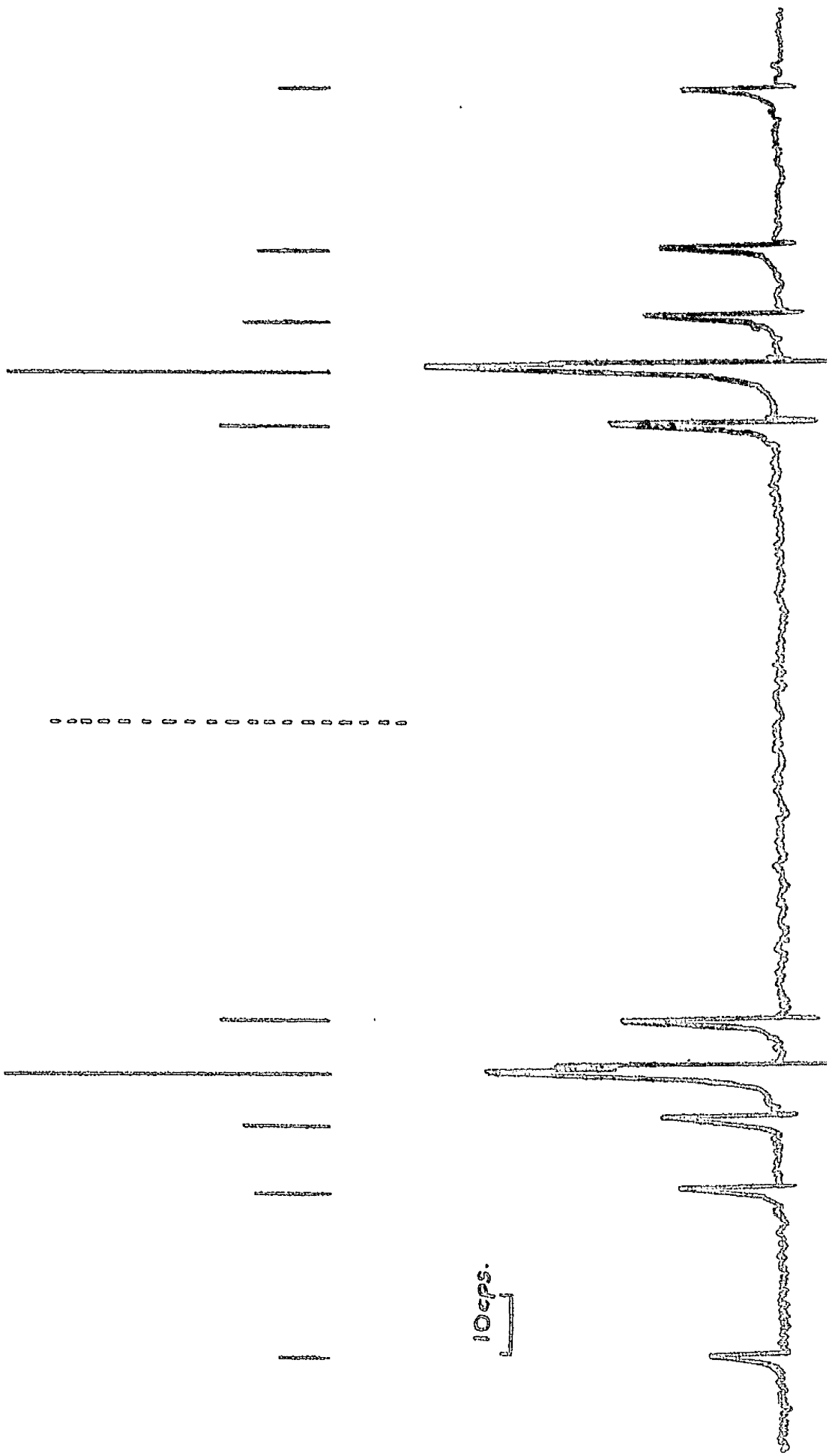
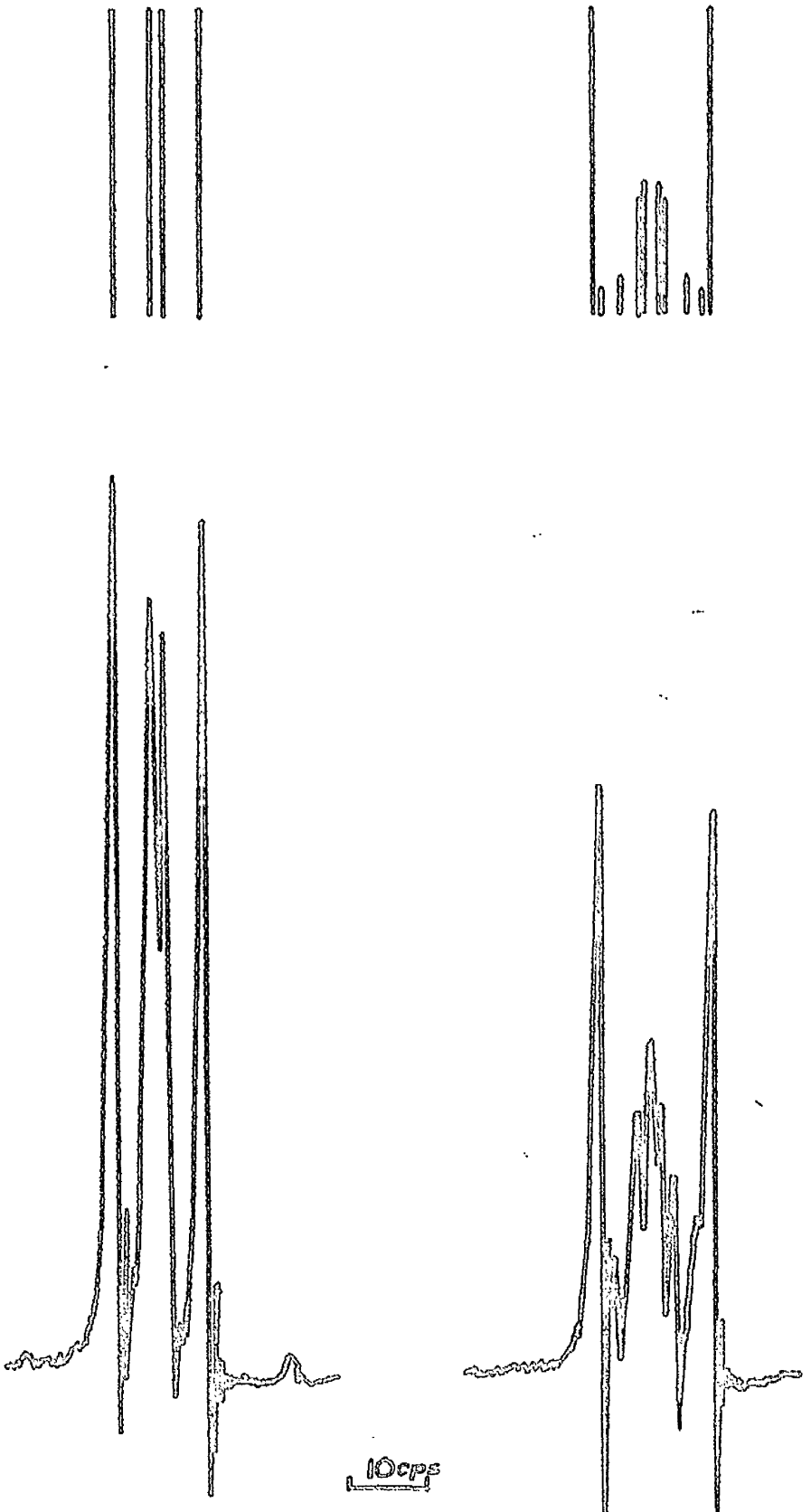
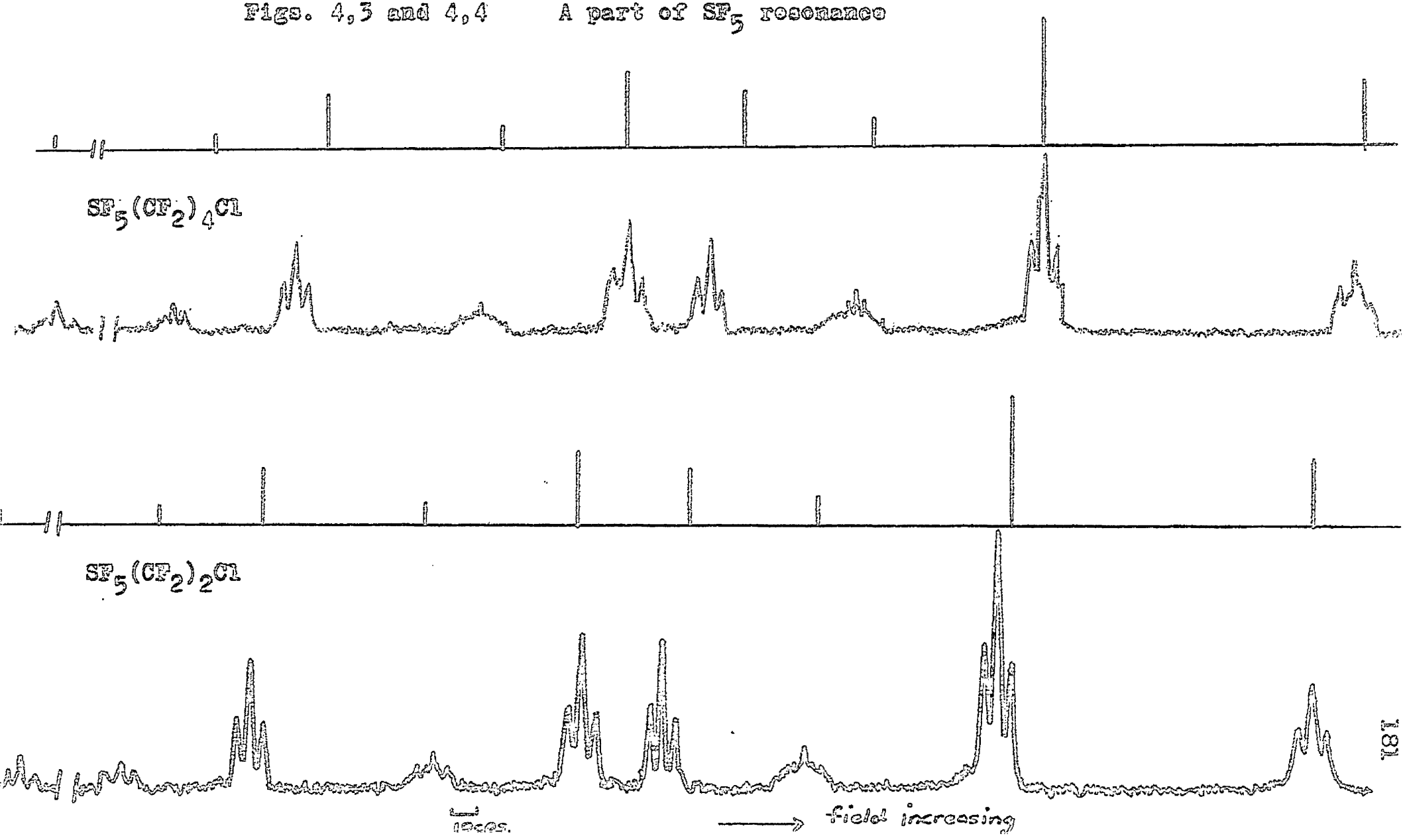


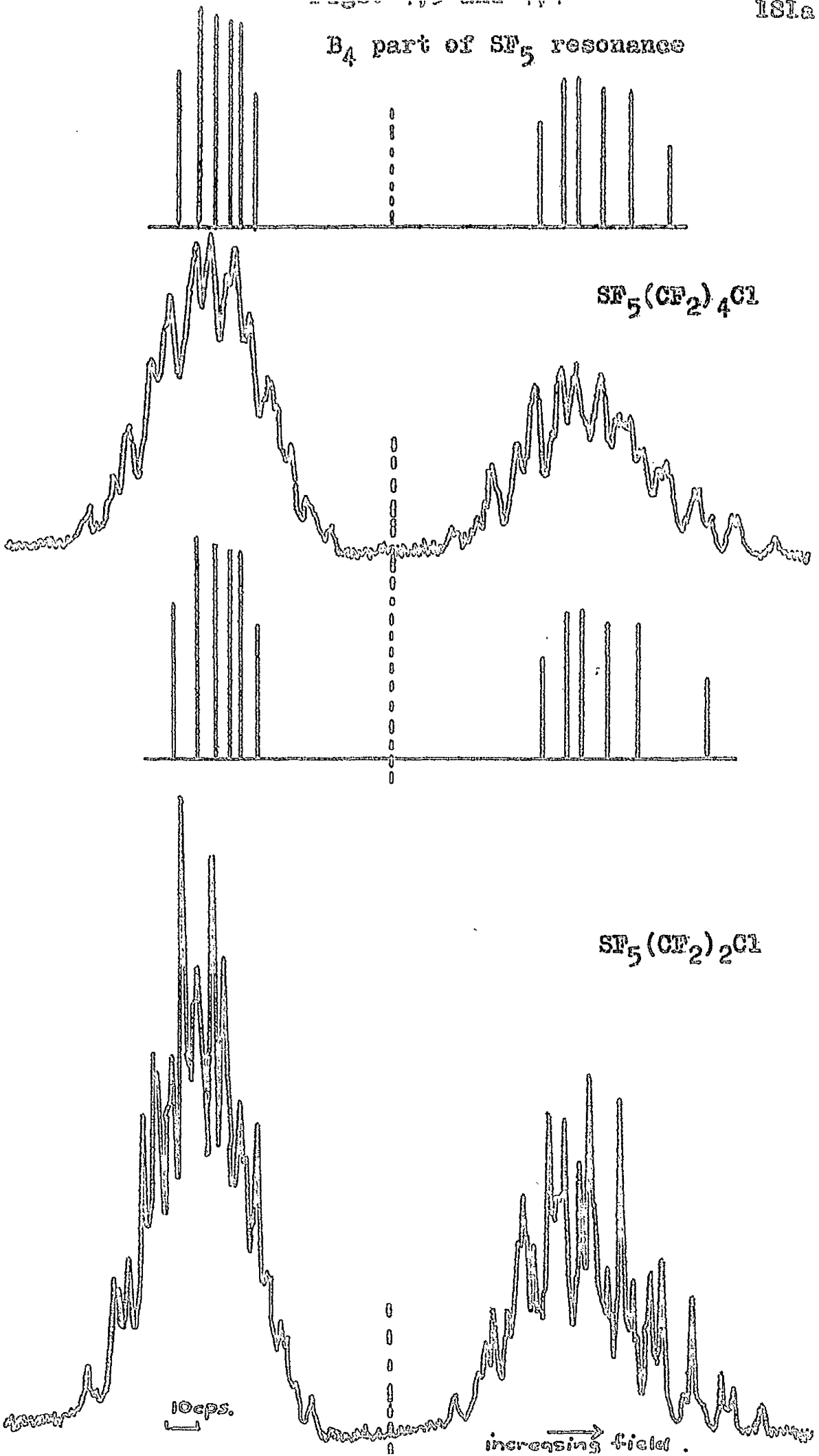
Fig. 4.1 Calculated A_2X_2 multiplet and lowfield multiplet of trans-trans $C_4Cl_2F_4$

Fig.4,2 Calculated and experimental low field multiplets of cyclo $C_4Cl_2F_4$ isomers



Figs. 4,3 and 4,4 A part of SF_5 resonance




B_4 part of SF_5 resonance
$SF_5(CF_2)_4Cl$
$SF_5(CF_2)_2Cl$
10cps.
increasing field

CHAPTER FIVE

SOME MOLECULAR COMPLEXES OF TRANSITION-METAL FLUORIDES

Introduction - Molecular Complexes

Compounds containing molecular species in a simple stoichiometric ratio are very extensive both in organic and in inorganic chemistry. One important class of these compounds are those between an aromatic or lone-pair containing organic molecule and an inorganic molecule. It is considered that such complexes are formed by electron transfer from the donor molecule(D) to the acceptor molecule(A).

Tungsten hexafluoride has been reported to form coloured solutions in organic solvents that contain π-electrons or lone pairs (PRIEST, SCHUMB 1948a). It has been suggested that these coloured solutions are due to charge transfer interaction between the donor organic molecule and the acceptor (WF_6). The present work was undertaken to examine the N.M.R. spectra of such solutions in order to obtain information about the species present. It was thought that the chemical shift of the ^{19}F nuclei in WF_6 would be a function of the donor molecule. By this means correlation between

the chemical shift and the donating power of the organic molecule could be obtained.

Methods Used to Study Donor Acceptor Complexes

Where a solid complex is formed its composition can be determined by analysis but when the complex is of low stability, and is formed only in solution, its presence can often be detected by a colour change or by a change in physical properties of one of the components (ANDREWS 1954). Solubility measurements (e.g. of HF in benzene) have provided evidence for complex formation (HAMMETT 1940) as have distribution studies of an acceptor between donor and non-donor solvents (McCAULAY, LIEN 1951).

Other methods that have been used include melting point composition diagrams (PLOTNIKOV, GRATSIANSKII 1945), dipole moments (FAIRBROTHER 1948) and infra-red spectra (GORDY 1941). Recently electron spin resonance has been used to show the presence of charge transfer complexes between organic donor molecules and $VOCl_3$ (KRAUSS, DEFFNER 1964).

The method most widely used to investigate donor-acceptor complexes is that of spectro-photometric measurements. BENESI and HILDEBRAND (1949) found a strong absorption band in the ultra-violet spectrum of a solution of iodine in benzene. This band was

absent in benzene itself and in solutions of iodine in non-donor solvents, so it was presumed to be characteristic of complex formation. Since then characteristic absorption bands have been found for many complexes (e.g. ANDREWS 1954).

Theory of the Bonding in Donor-Acceptor Complexes.

The most complete theory of the bonding in donor-acceptor complexes was developed by MULLIKEN (1952) to explain the presence of the new absorption band in their ultra-violet spectra. The theory has since been modified (see McGLYNN 1958; MULLIKEN, PERSON 1962) but in essence it remains the same. The interaction of an electron donor (D) with an acceptor (A) is described in terms of resonance between 'no-bond' (DA) and ionic (D^+A^-) structures. The 'no-bond' structure is one in which interaction takes place by classical intermolecular forces e.g. dipole-dipole or dipole-ion interactions. The ionic structure is that in which an electron has been transferred from one species to the other (the most important canonical structure involves electron transfer from the donor to the acceptor). The wave equation $\psi_N(D,A)$ for the ground state of the complex is given by equation 1.

$$\psi_N(D,A) = a\psi_0(DA) + b\psi_1(D^+A^-) \qquad (1)$$

$\psi_0(DA)$ and $\psi_1(D^+A^-)$ are wave functions corresponding

to the 'no-bond' and ionic structures respectively. The ratio b:a determines the contribution of the ionic structure to the ground state and this is usually small. If the donor is a weak base and the acceptor a weak acid, electron transfer from the acceptor to the donor becomes significant (MULLIKEN 1954) and a third term $\psi_2(D^-A^+)$ is added to the wave equation of the ground state (equation 2).

$$\psi_N(D,A) = a\,\psi_0(DA) + b\,\psi_1(D^+A^-) + c\,\psi_2(D^-A^+) \qquad (2)$$

Where $a > b \gg c$. The presence of the third term complicates the calculation of energy levels so equation 1 has been used in quantitative treatments.

The wave equation of the first excited state, $\psi_E(D,A)$, corresponding to equation 1 is given by equation 3 (ORGEL 1954).

$$\psi_E(D,A) = a\,\psi_1(D^+A^-) - b\,\psi_0(DA) \qquad (3)$$

The ionic contribution to the ground state is small so the covalent contribution to the excited state will be small. Electronic transitions between the two states are responsible for the 'charge transfer' absorption band characteristic of a complex. Other things being equal, a reduction in the ionisation potential of the donor or an increase in the electron affinity of the acceptor, leads to an increase in the ionic contribution to the ground state and to the stability of the complex.

Empirically it has been found that a plot of the 'charge transfer' frequencies against the ionisation potentials of the donors, for a series of complexes having a common acceptor, is linear (e.g. McCONNELL, HAM, PLATT 1953), although this is a simplification of the theory (McGLYNN 1958).

MULLIKEN'S theory predicts that the extinction coefficient of the charge transfer band should increase with increasing equilibrium constant of the complex (MULLIKEN 1956) but the reverse is found for π donor complexes (e.g. McGLYNN 1958). It has been suggested (ORGEL, MULLIKEN 1957) that this can be explained by a contribution from contact charge transfer interactions, originally proposed by EVANS (1955). These authors have examined a model of the I_2/C_6H_6 solution that supposes the solution to consist of a definite fraction of saturated 1:1 complexes of relatively low energy and of relatively favourable orientation. Each of these is surrounded by non-interacting benzene molecules, plus the remaining fraction of I_2 molecules that have random contact charge transfer interactions with the benzene molecules. In reality there must be a continuous gradation from actual complexes of different geometries to loose contacts having differing orientations and stoichiometry.

The Mulliken theory also predicts that a complex will have a preferred orientation, such that the overlap integral of the ground state wave function is a maximum (MULLIKEN 1956). Structural work on several solid donor-acceptor complexes has confirmed this (MULLIKEN, PERSON 1962).

^{19}F N.M.R. Resonance in Binary Fluorides

The chemical shifts of a large number of binary non-transition element fluorides can be explained qualitatively by variations in the paramagnetic term of the shielding equation (SAIKA, SLICHTER 1954). The ^{19}F resonance is progressively displaced to lower field as the atomic number of the central atom in a given period of the periodic table increases. A general correlation exists between the ^{19}F chemical shift and the Pauling electronegativity of the central atom, for a given period (GUTOWSKY, HOFFMAN 1951); the ^{19}F resonance occurs at lower field with increasing electronegativity of the heteroatom. The same effect is found for corresponding fluorides in a given main group e.g. the shielding increases in the order $NF_3 < AsF_3 < PF_3 < SbF_3$.

Little work has been reported for transition metal fluorides but in the series MoF_6, WF_6 and UF_6, the shielding increases with an increase in electronegativity

of the metal. The large low field shift experienced by UF_6 is thought to be due to the presence of low lying excited states (SILBIGER, BAUER 1946).

The frequency of the octahedral ν_3 vibration in WF_6 is greater than that in MoF_6 (GAUNT 1953; CLAASSEN, SELIG, MALM 1962) indicating that the bond strength increases in going from MoF_6 to WF_6. It has been suggested (GOODMAN 1963) that this reflects an increase in π-character of the W-F bond compared to the Mo-F bond.

There would seem to be another factor, possibly molecule-molecule attraction in the liquid state, that determines the magnetic shielding in MoF_6 and WF_6.

The magnitudes of the M-F coupling constants (where M is a magnetic nucleus) reflect a radical change in the hybridisation of M rather than substitution effects for a given hybridisation. For example the ^{19}F-^{31}P and ^{19}F-^{29}Si coupling constants in phosphorus and silicon fluorides are affected by the hybridisation of the P and Si atoms (MUETTERTIES, PHILLIPS 1959) but ^{19}F-^{31}P coupling constants are fairly constant for a large number of octahedral base -PF_5 complexes (MUETTERTIES, BITHER, FARLOW, COFFMAN 1960).

^{19}F N.M.R. Spectra of the Solutions Prepared in the Present Work

The N.M.R. spectra of solutions of WF_6 in benzene, toluene, hexafluorobenzene, diethyl ether and carbon tetrachloride and of MoF_6 in hexafluorobenzene were studied. The colours of the solutions and the parameters obtained from the hexafluoride resonance are shown in Table V,1.

The signals due to WF_6 observed in the solutions (except Et_2O) were identical with that observed in liquid WF_6, a single peak with two sidebands whose intensity was approximately 15% of the total signal intensity. The side bands arise from ^{19}F nuclei bound to the ^{183}W nucleus (spin $\frac{1}{2}$, abundance 14.28%) and their separation equals the value of the ^{19}F-^{183}W coupling constant. The signal due to MoF_6 in C_6F_6 was the same as that in liquid MoF_6, namely a single peak with six side bands. The latter arise from ^{19}F nuclei bonded to ^{95}Mo and ^{97}Mo nuclei (both nuclei have spin 5/2, their abundance being 15.78 and 9.60% respectively). Sidebands due to the separate nuclei were not observed, as the spectra were broadened by quadrupole relaxation of the high spin nuclei, and because the nuclei have similar magnetogyric ratios.

The values of the coupling constants obtained are

an average of the ^{19}F-^{95}Mo, and ^{19}F-^{97}Mo values.

The spectra of liquid WF_6 and MoF_6 have been reported previously (MUETTERTIES, PHILLIPS 1959); the parameters obtained were as follows: WF_6 at -165ppm., ^{19}F-^{183}W = 48cps.; MoF_6 at -278ppm., ^{19}F-(^{95}Mo, ^{97}Mo) = 44cps. There are small differences between these values and those obtained in the present work.

The solvent resonance of the WF_6 solutions was essentially the same as that of the pure liquid. Very small upfield shifts of the benzene and toluene signals were observed, but these were less than the experimental error in the measurements. The spectrum of MoF_6/C_6F_6 in the aromatic fluorocarbon region consisted of two peaks, a very strong peak at +163.9ppm. and a weak peak at +177.3ppm. The spectra of the WF_6/C_6F_6 solutions in the same region each consisted of a single peak (at +163.5 and +163.8ppm. respectively). The chemical shift of C_6F_6 (30% solution in CCl_4) is +163.1ppm.

The ^{19}F spectra of WF_6/Et_2O solutions did not contain a signal characteristic of WF_6 but showed a broad, featureless signal of low intensity. The peak width at half height was 7.3cps. The spin-lattice relaxation time (T_1) of the ^{19}F nuclei in this solution must be considerably smaller than those in the other solutions examined. The local field fluctuations that

Table V.1

Spectral parameters of MF_6 resonance in various solvents

solution	colour at 20°C.	approx. concentration $g.cm^{-3}$	^{19}F chemical shift ppm. from CCl_3F	M-^{19}F coupling constant (cps)
WF_6/C_6H_6	red	0.8	-165.9	41.9
"	"	"	-166.4	43.3
"	orange	0.02	-166.3	40.4
WF_6/C_7H_8	red	0.8	-164.9	44.4
"	"	"	-166.4	41.8
WF_6/C_6F_6	yellow	0.8	-165.3	43.9[5]
"	2	"	-165.3	44.4
WF_6/Et_2O	yellow	0.7	-164.7	-
"	"	"	-163.8	-
WF_6/CCl_4	colourless	0.4	-165.3	42.3
"	"	"	-165.6	41.2
"	"	"	-166.2	41.1
WF_6	colourless	-	-164.8	43.6[5]
MoF_6/C_6F_6	dark red	2.7	-283.0	47.4
MoF_6	colourless	-	-282.4	47.2

are effective in spin-lattice relaxation are increased by the addition of paramagnetic species so T_1 is shortened. A reduction in T_1 is accompanied by a similar reduction in the spin-spin relaxation time (T_2) and this results in a broadening of the signal and a decrease in the peak height (RICHARDS 1962).

Discussion of the Spectra Obtained

In all the solutions studied, except WF_6/Et_2O, a downfield shift of the $WF_6(MoF_6)$ signal relative to the liquid hexafluoride was observed. This shift was very small (0-1.5ppm.) and is of the same order as the 'solvent effect' which is well known in ^{19}F chemical shifts. A downfield shift of the ^{19}F resonance of a fluorine compound occurs in many solutions, compared to that of the pure liquid or gas. The magnitude of the shift depends upon the solvent. There must be an increase in the paramagnetic shielding term of an ^{19}F nucleus in solution but it is too great to be accounted for solely by changes in the volume susceptibilities of the solvents. It has been found (EVANS 1960) that an approximate linear relationship exists between the solvent shift and its refractive index. The latter is a function of the polarisability of the solvent and its molecular volume. A correlation between the solvent effect and molar polarisability has been found using

halogenomethanes as solvents (GLICK, EHRENSON 1958). In this case the sizes of the solvent molecules are similar.

Complex formation is inferred where the solutions are coloured but any charge transfer interaction has little effect on the chemical shifts. The downfield shifts in the C_6H_6 solutions are greater than those in the CCl_4 solutions, where no interaction occurs. For a large number of organic fluorine compounds the CCl_4 solvent shift is greater than that for C_6H_6 (EVANS 1960). This might mean that the charge transfer interaction contributes to the downfield shift. However, the chemical shifts of WF_6 in these solutions depend on the concentration and this effect will have to be evaluated before different solutions can be compared.

The solvent spectra give little information except for the MoF_6/C_6F_6 spectrum. The two peaks obtained suggest that the C_6F_6 molecules can exist in two environments that have an exchange frequency smaller than their frequency difference. Alternatively the high-field peak could be due to another species, in which all the ^{19}F nuclei are equivalent.

The ^{19}F signal in the WF_6/Et_2O solutions is shifted upfield from pure WF_6. Small upfield shifts of the resonance due to organic fluorine compounds occur in ether solutions (EVANS 1960). The signal shape of the

WF_6/Et_2O solutions suggests the presence of a paramagnetic species that affects the ^{19}F nuclei relaxation time but not that of the ether protons.

The N.M.R. spectra are consistent with the fact that, except for WF_6/Et_2O, the solutions contain WF_6 or MoF_6 and not any lower valency states of the elements. It has been reported (PRIEST, SCHUMB 1948a) that the stoichiometry of the WF_6/C_6H_6 complex is 1:1 This was suggested as the optical densities of CCl_4 solutions of the complex varied directly with the concentration of either reactant, although no figures were reported. The WF_6 and MoF_6 signals indicate that all the ^{19}F nuclei are equivalent. The constancy of the M-F coupling constants suggests that octahedral symmetry is preserved in solution. However, a complex similar to the model described by ORGEL and MULLIKEN (1957) would grant equivalence to the ^{19}F nuclei and preserve a formal octahedral symmetry, providing the exchange frequencies were high.

The small effect of the charge transfer interaction on the ^{19}F chemical shift of the hexafluorides may be due to the fact that the interaction is essentially between the organic donor and the metal atom, the electron distribution around the ^{19}F nuclei being hardly affected.

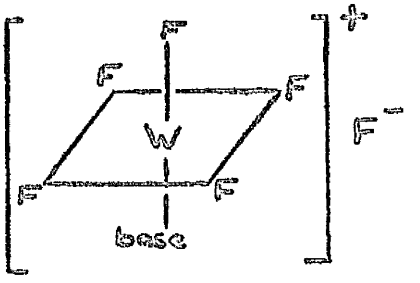
An alternative explanation is that an equilibrium exists between a complex formed with a reduced W or Mo species and the donor organic molecule and the 'uncomplexed' hexafluoride and solvent molecules. The colour of a solution would be due to the reduced species but the equilibrium would favour the uncomplexed species. If the relaxation time of the ^{19}F nuclei in the 'reduced complex' were very small the signal due to this might not be observable. A reduced W species seems to be formed in the WF_6/Et_2O solution where the colour of the solution changes with time.

Some Reactions of Metal Fluoride Complexes

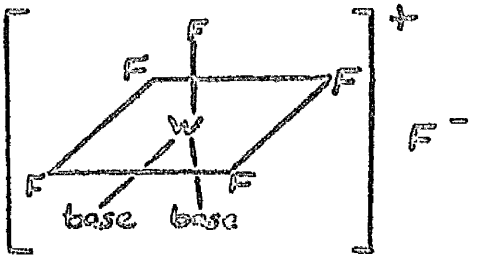
The colours of the solutions prepared indicate that the equilibrium constants of WF_6/C_6F_6 and WF_6/C_7H_8 are greater than that of WF_6/C_5F_6 and that the equilibrium constant of MoF_6/C_6F_6 is greater than that of WF_6/C_6F_6. Thus C_6H_6 is a better electron donor than C_6F_6. A solid molecular 1:1 complex between C_6H_6 and C_6F_6 has been reported (PATRICK, PROSSER 1960) but no new absorption band was found in the range 2300-3000^{0}A.

Both WF_6 and MoF_6 exhibit acidic properties in liquid hydrogen fluoride (CLIFFORD, BEACHELL, JACK 1957) and a series of 1:1 and 2:3 complexes between WF_6 and strong organic bases (e.g. PPh_3, NMe_3) has been prepared (MUETTERTIES 1961). On the basis of their N.M.R. spectra

and from conductivity measurements ionic structures (I or II) have been postulated for these compounds. Structure I is thought to be most likely as solvation of the ions by the donor molecules is possible.



(I)



(II)

The ^{19}F-^{183}W coupling constants in these complexes are ~72cps. This reflects a change in W-F bond hybridisation compared to that in WF_6 and its solutions. A 2:1 adduct between pyridine and MoF_6 has been reported (MUETTERTIES 1961) but its structure is not known.

An attempt was made to prepare a solution of WF_6 in tetrahydrofuran (THF) but the latter was readily polymerised at 20°C. THF is readily polymerised in the presence of PF_5 (SIMS 1964) and it has been suggested that the ability to act as a polymerisation catalyst is a function of the acceptor properties of the molecule (WOOLF 1956). The THF polymer turned blue on exposure to air suggesting that some reduction of W(VI) to W(V) had occurred. Evidence for the reduction of W(VI) was also obtained from the ether/WF_6 solution.

The colour of this solution had been reported to be violet-brown (PRIEST, SCHUMB 1948a) but when freshly prepared it was yellow. The solution became darker after several hours, eventually precipitating out a brown solid. No evidence for the presence of fluorinated organic compounds in the volatile product was obtained but the dark blue solid, remaining after the volatile material had been removed, hydrolysed in water to give a blue solution.

Tungsten tetrafluoride has been prepared by the reaction of WF_6 with C_6H_6 at 110°C. for several days in a bomb (PRIEST, SCHUMB 1948b). This reaction was repeated to examine the volatile products. A brown tar, which appeared to contain carbon and benzene resulted from the reaction. It appears that the reduction of WF_6 by organic donor solvents does not lead to a smooth fluorination of the organic molecule.

The solutions WF_6/C_6H_6, C_7H_8 and C_6F_6 were stable over long periods in the absence of moisture. If WOF_4 was present however, decomposition occurred and it seems that WOF_4 is more easily reduced than is WF_6.

MoF_6 is very easily hydrolysed to give blue solutions (NIKOLAEV, OPALOVSKII 1959) and on the evidence available it is a better acceptor than WF_6 (GEICHMAN, SMITH, TROND, OGLE 1962). Little chemistry of MoF_6 is

known, partly due to the fact that rigid precautions must be taken when handling it to exclude water (O'DONNELL 1956). It is hoped that the use of C_6F_6 as a solvent for MoF_6 will enable its chemistry to be extended and future work along these lines is planned. A sample of MoF_6/C_6F_6 was stored at $0^oC.$ for several days without decomposition.

The formation of coloured solutions when covalent fluorides are dissolved in organic donor solvents may be quite general. $(SeF_5O)_2Te_2F_{10}$ and $F_5TeOTeF_4OTeF_5$ been reported to form strongly coloured solutions in benzene, α-naphthylamine and pyridine (MITRA, CADY 1959). Also a solution of TaF_5 in C_6F_6 was prepared in the present work. The colour of this solution varied with its concentration, from indigo at high concentration to green at lower concentration. It is hoped to study the N.M.R. spectra of this and similar solutions.

Conclusion

Solutions of WF_6 in benzene, toluene and hexafluorobenzene and of MoF_6 in hexa fluorobenzene are strongly coloured. The evidence obtained suggests that the colours are due to 'charge transfer' interaction between the organic molecules and the hexafluoride and not to the presence of a lower valency state of the metal. The effect of solution on the hexafluoride ^{19}F chemical

shift is small and of the same order as a normal solvent effect. This may mean that the interaction is essentially between the metal and the organic molecules. It seems likely that such solutions will provide useful reaction media and will enable the spectroscopic study of solid fluorides to be undertaken in solution.

EXPERIMENTAL

Preparation of the Fluorides

Tungsten, molybdenum hexafluorides and tantalum pentafluoride were prepared by reaction of the metal with fluorine using standard procedures (PEACOCK 1960). WF_6 and MoF_6 were purified by vacuum distillation and stored in breakseal flasks over sodium fluoride at -180°C. Tantalum pentafluoride was purified by repeated sublimation.

Purification of the Solvents

The solvents were all from commercial sources. Benzene, toluene and diethyl ether were dried over sodium before use; carbon tetrachloride and hexafluorobenzene were dired over activated molecular sieves (B.D.H. 5A). To purify the solvents further, they were degassed and distilled twice at low temperatures under vacuum, taking the middle fraction each time. The following distillation temperatures were used:
C_6H_6 -20°C; C_7H_8 -50°C; $(C_2H_5)_2O$ -78°C; C_6F_6 -50°C; CCl_4 -30°C.

Experimental Method

A small quantity of the solvent required was distilled into a trap on an all glass manifold, to which a number of breakseal flasks and the breakseal flask containing the fluoride had been already sealed. The

seal on the flask containing the fluoride was broken and the fluoride distilled onto the solvent at -196°C. (It was necessary to sublime TaF_5 using a bunsen flame). The mixture was allowed to warm up to room temperature and any reaction to take place. The mixture was then distilled at 20°C. and sealed up in breakseal flasks. These samples were transferred to pyrex N.M.R. tubes by vacuum distillation through another all glass manifold. Diagrams of the apparatus used are shown in the appendix.

The concentrations of the solutions were not determined accurately, although approximate values were obtained from the weight of metal used in the fluorination (assuming an 80% yield), the volume of solvent before distillation, and the volume of solvent rejected from the distillations.

^{1}H and ^{19}F N.M.R. spectra were observed under the same conditions as already described. Tetramethylsilane (TMS) and CCl_3F were used as internal references for the WF_6 solutions. It was found that the MoF_6 prepared contained a small amount of WF_6 as impurity; the latter was used as an internal reference for the MoF_6 spectra. The MoF_6 resonance occurred outside the range of the field sweep of the spectrometer so a 10,000cps. upfield sideband of the signal (generated using a Muirhead oscillator) was used to measure the

chemical shifts and coupling constants. All parameters quoted are the average values from several spectra.

Description of the Solutions Obtained

Benzene and Tungsten Hexafluoride. When WF_6 was distilled on to C_6F_6 at -196°C. an orange solid was obtained. At -78°C. this solid was colourless but on warming to 20°C. a red liquid was obtained. This colour was very intense; even at a concentration of 50mg. of WF_6 in 3ml. of benzene, the colour of the solution was orange. These solutions were stable in the absence of moisture and could be kept for several months without decomposition.

On one occasion when the complex was allowed to warm up to 20°C. a small quantity of solid material, in addition to the red solution, was observed. A sample of this mixture was sealed up and allowed to stand at 20°C. for two days. Examination of the products showed that the most volatile fraction was a mixture of SiF_4 and COF_2. An infra-red spectrum of the fraction contained bands characteristic of COF_2 and SiF_4 (NIELSEN, BURKE, WOLTZ, JONES 1952; JONES, KIRBY-SMITH, WOLTZ, NIELSEN 1951). The 'molecular weight' of the fraction was 92.2 (M.W. of COF_2=66.0; M.W. of SiF_4=104.1) A small quantity of the red solution was distilled off leaving a dark brown solid. This fumed in air and was

hydrolysed in water to give a dark blue solution. Reduction of the tungsten had taken place (to W(V)), the reaction probably being due to the presence of WOF_4 as an impurity in WF_6.

A sample of the WF_6/C_6H_6 red solution (ca 1ml.) was distilled in to a stainless steel bomb (as described in Ch.1) under vacuum and allowed to react at 110°C. for 4 days. The volatile product was a colourless liquid whose infra-red spectrum was identical with that of benzene. The bomb was opened in the dry-box and contained a dark brown viscous liquid. This fumed in air and was oxidised by conc. HNO_3 giving a yellow precipitate (WO_3) and a black solid (carbon). An infra-red spectrum of the sample showed the presence of aromatic C-H and C=C bands but there were no bands that could be definitely assigned to C-F vibrations. No evidence was found for any volatile products containing fluorine.

Toluene and Tungsten Hexafluoride at -196°C. gave an orange solid and a red solution on warming to 20°C. There was no transition through a colourless solid on warming.

Hexafluorobenzene and Tungsten Hexafluoride produced a yellow solid at -196°C. This remained yellow until melting took place to give a yellow solution.

Diethyl Ether and Tungsten Hexafluoride gave a yellow

solid at -196°C. and on warming to 20°C. a yellow liquid was produced. This darkened when it was allowed to stand in a breakseal flask at 20°C. for several hours and after several days a brown solid was precipitated. The flask was resealed to the vacuum line and its contents examined. A colourless liquid was distilled at 20°C., the infra-red spectrum of which showed bands consistent with SiF_4 and $(C_2H_5)_2O$ (PIERSON, FLETCHER, GANTZ 1956). The involatile product was a viscous, dark brown liquid. When this was heated at 100°C. in vacuum, a small quantity of ether was evolved, leaving a dark blue solid. This was rapidly hydrolysed in moist air to give a dark blue solution.

N.M.R. spectra of the yellow ether solutions were taken immediately after their preparation, before any darkening had occurred.

Carbon Tetrachloride and Tungsten Hexafluoride gave a colourless solution at 20°C. Providing no moisture was present, there was no fluorination of CCl_4.

Tetrahydrofuran and Tungsten Hexafluoride THF was readily polymerised by WF_6 at 20°C. On exposing the polymer to moist air it turned blue, suggesting that reduction of tungsten had occurred.

Hexafluorobenzene and Molybdenum Hexafluoride gave a red solid at -196°C., which melted to a dark red solution

on warming to 20°C. The stability of the complex towards water was considerably less than that of $WF_6.C_6F_6$, only traces of water absorbed on the glass being necessary to cause hydrolysis. When this occurred, a colourless liquid and a blue solid were produced. Solutions stored at 0°C. in N.M.R. tubes, which could not be thoroughly flamed out due to possible distortion, started to hydrolyse after 12 hours. Samples stored in breakseal flasks at 0°C. could be stored for longer periods.

Hexafluorobenzene and Tantalum Pentafluoride gave a dark blue solid at -196°C. which resulted in an indigo solution, that contained some solid material, at 20°C. On distilling more C_6F_6 into the mixture, the solution turned green and no solid remained. The colour of a very dilute solution was pink. Removing C_6F_6 by distillation reversed these colour changes.

APPENDIX

APPARATUS USED IN THE COURSE OF THE WORK

Vacuum Apparatus Used

All volatile compounds (except those described in Chs.3 and 4) were handled in a glass vacuum line equipped to separate mixtures of volatile compounds, to determine their molecular weights and to prepare samples for gas infra-red and liquid high resolution nuclear magnetic resonance spectroscopy. The line was assembled from shoft glass manifolds, using standard ground glass joints greased with Apeizon L. The line was flamed out as far as possible before use. Although the vacuum obtained from this system is less than that obtained from an all glass system, cleaning the line after a 'dirty' reaction is easier. Using a rotatory oil pump and a mercury diffusion pump in series, a vacuum of 10^{-4}mm or better could be obtained. The all glass fractionation train is shown in Fig.1. By repeated distillations through the U-trap, complete separation of compounds of different volatility (e.g. a mixture of $C_6H_5PF_4$ and PF_5) was possible.

Gaseous infra-red spectra were taken in a 10cm. gas

cell (from Research and Control Instruments Ltd.) using sodium chloride optics. Gas pressures were measured by a manometer. Samples for nuclear magnetic resonance spectroscopy were distilled into pyrex sample tubes sealed to an all glass manifold (Fig.2). When a solvent and internal reference were used, these were distilled into the tube under vacuum. Compounds that were very unstable to water or that reacted with grease, were stored and transferred to and from the line in breakseal flasks. (Fig.3).

Molecular weights of volatile compounds were determined by weighing a known volume of vapour at a measured pressure and temperature. The weight of vapour that would occupy the gram molecular volume at N.T.P. was then calculated. The weighing bulb used was similar to that described by Sanderson (1948) and is shown in Fig.4. Vapour pressures were measured using a manometer from a design due to Dr. K. K. Joshi, shown in Fig.5. The manometer consists of a glass U-tube about 70cm. in length with a mercury reservoir at one end. The seal at F is made by a ground glass joint with a small quantity of mercury above it.

Filling the manometer

The manometer was evacuated and thoroughly flamed out. The reservoir was filled with mercury (previously

cleaned with 5% nitric acid and dried) at E, the plunger lifted and mercury allowed to fall into the U-tube. The capillary tubing prevents the mercury from breaking the glass when it falls. This process was repeated until a suitable column was obtained. However, efficiently the manometer is flamed out, some air is always present in the space above A. To remove this a Torrichelian vacuum was created by letting air to the vacuum system, thus pushing the mercury to FC. The column was frozen at C with a plug of cotton wool soaked in liquid air, DC was evacuated and flamed out. The column was allowed to warm up and fall back to AB, trapping a mercury thread in the capillary at F with the air above it. The manometer was then ready for use.

Calibration of the weighing bulb

This was effected using carbon dioxide. A quantity of CO_2 vapour was introduced into the vacuum line and dried by distillation at -80°C. The bulb was filled with CO_2 at several different pressures from 70mm to 270mm. The volume of the bulb was found to be $68.3 \pm 0.2 cm^3$. The molecular weight is given by the expression $912.4 \frac{WT}{P}$ where Wg. is the weight of vapour at a temperature of T°A and a pressure of P mm.

In determing the molecular weight of an unknown the pressure was measured to 0.5mm., the weight of

vapour to 0.05mg. and the temperature to 0.5°. The accuracy of the determination therefore depended upon the weight of vapour in the bulb and its vapour pressure. When these were large compared to the error in measurement good results (i.e. to within 1%) were obtained. However in all cases where a pressure could be recorded, determination of the molecular weight of the vapour together with other evidence (e.g. infra-red spectrum or analysis), provided identification.

Other Apparatus Used

Infra-red spectra were recorded using a Grubb-Parsons S.4 or a Perkin Elmer Infracord spectrometer using NaCl optics and on a Grubb-Parsons DM2 spectrometer using CsI optics. Solid samples were run as mulls using NaCl plates or polythene discs and nujol or hexachloro-butadiene as mulling agents where appropriate.

Solid compounds that were unstable to water were handled in a Lintott dry box using P_2O_5 as desiccant or in a nitrogen bag that could be evacuated and then filled with dry nitrogen.

X-ray powder photographs were taken using Cu Kα radiation with a 9cm. van Arkel camera (from Unicam Instruments Ltd.). The samples were mounted in Lindemann tubes, which were sealed at one end with warm hydrocarbon wax.

Microanalyses were performed by the Micro-analytical Department, University of Strathclyde, and by the Alfred Bernhardt Micro-analytical Laboratories, Germany.

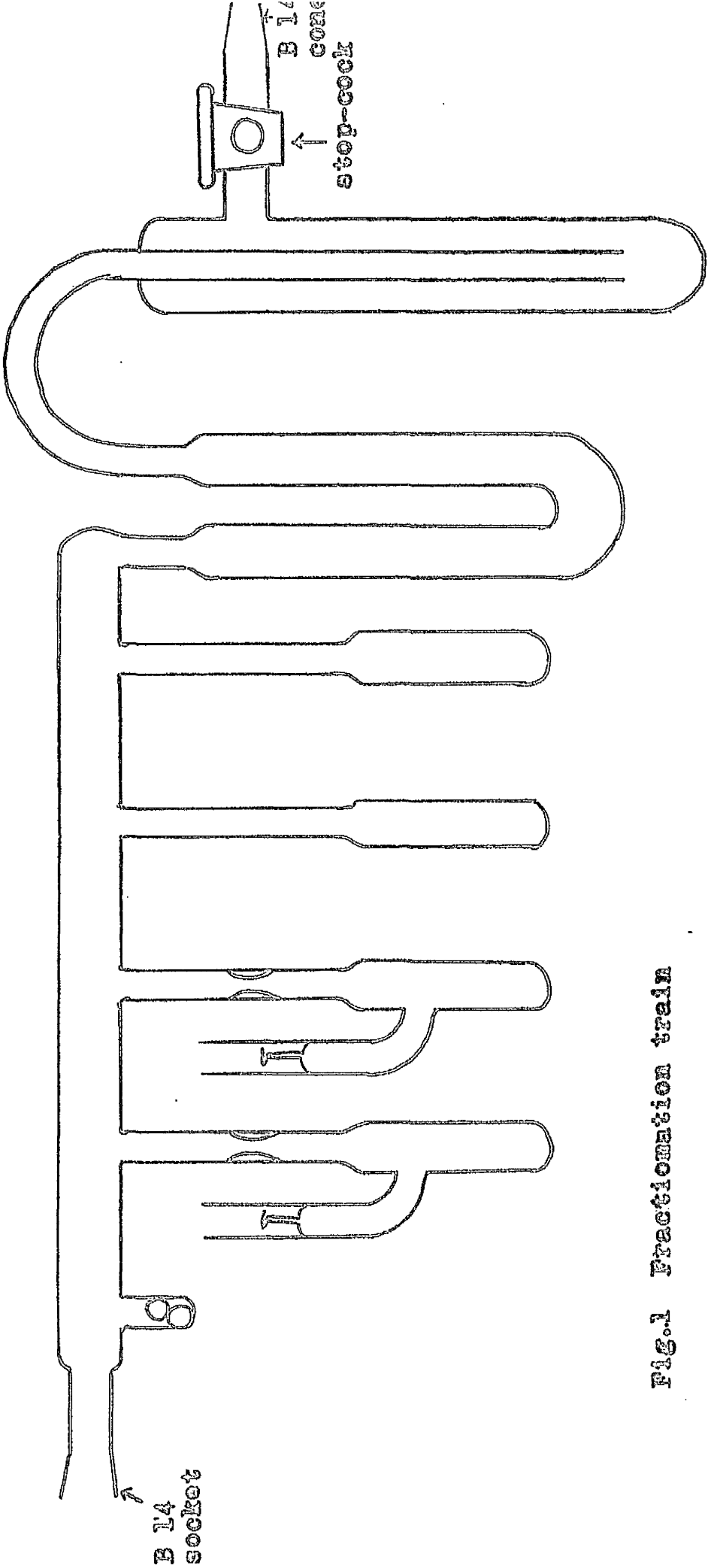


Fig.1 Fractionation train

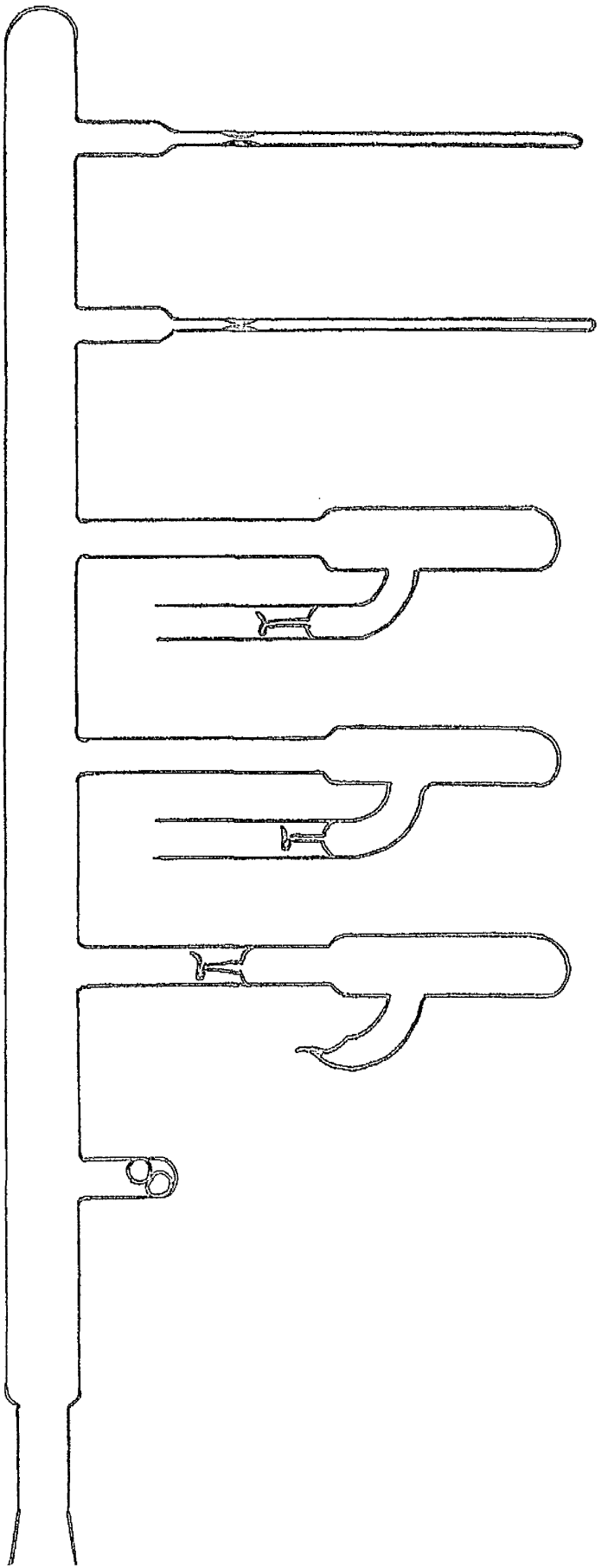


Fig.2 N.M.R. glass manifold

Fig.3

Breakseal flask

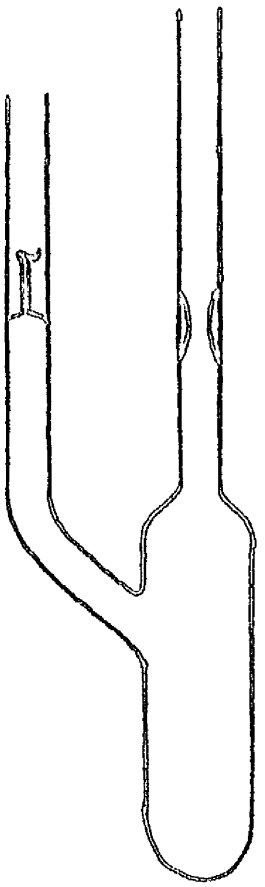
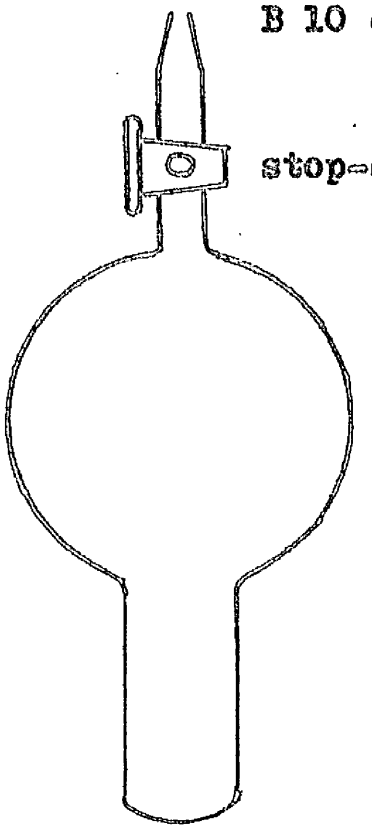


Fig.4

Molecular weight bulb



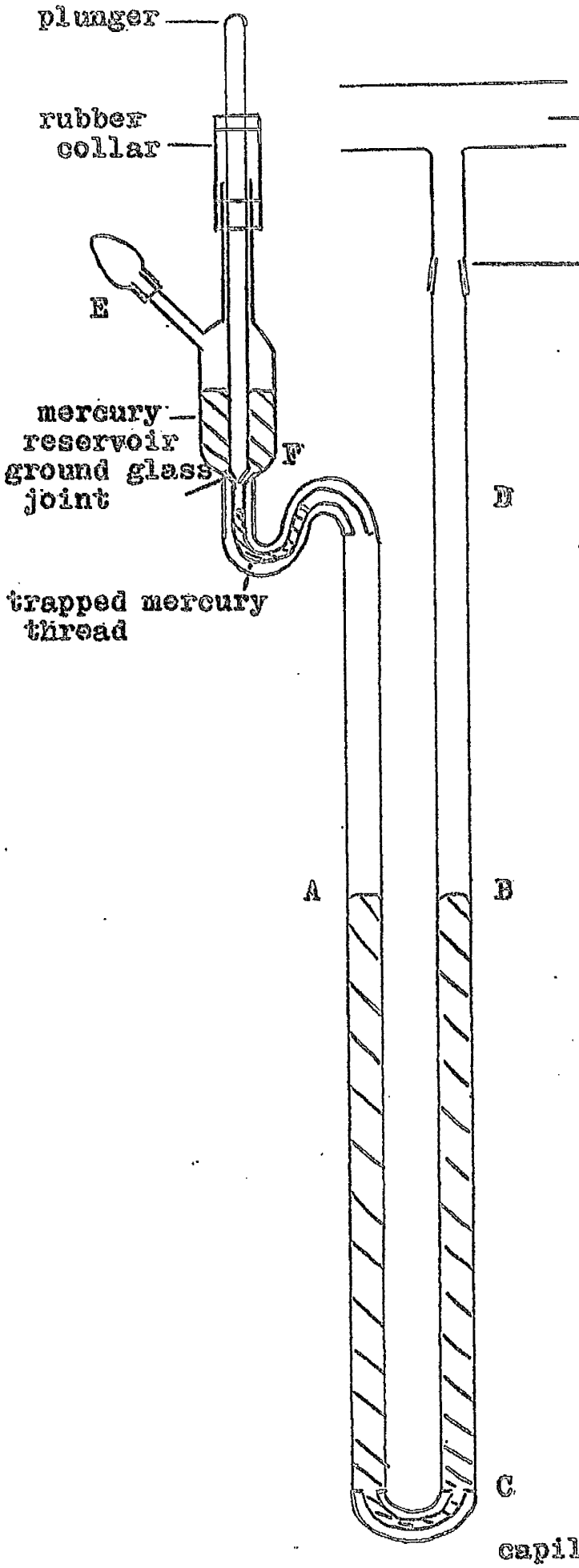


Fig.5 Manometer

Dimensions

CD 65cm.

tube diameter 0.9cm.

reservoir length 5cm.

reservoir diameter 3cm.

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